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SYSTEMATIC INVESTIGATION OF NONAQUEOUS SWELLING AGENTS FOR COTTON CELLULOSE

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SYSTEMATIC INVESTIGATION OF NONAQUEOUS SWELLING AGENTS FOR COTTON CELLULOSE

by

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Textile Research Institute

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ABSTRACT

A wide variety of single component and binary nonaqueous systems were investigated by several methods in order to assess the ability of these systems to penetrate, interact, and swell cotton cellulose. Liquid of imbibition, fiber length, yarn contraction, differential dyeing, mechanical properties, and chemical reactivity measurements were made in order to characterize the various systems. A number of aqueous systems were investigated for comparison purposes.

It was found that the introduction of certain solutes, such as citric acid, urea, tartartic acid, and polyhydric alcohols into non-interacting solvents increased the interaction between the nonaqueous system and the cotton cellulose. The experimental results also indicated that molecular shape is of extreme importance in terms of the ability of a system to interact with cotton cellulose. Other experiments suggested that the concept of forming a cellulose derivative and subsequently removing the added group in order to form a more open or reactive structure seems to hold some promise. It was also observed that mercerized (aqueous) cotton which was dried by an organic solvent replacement technique gave evidence of greater reactivity than a mercerized sample dried by the normal heating method.

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CHAPTER I. INTRODUCTION

Chemical and physical modifications of cotton to impart desirable characteristics to fibers, yarns, or fabrics have become of increased importance. It is such modifications which have enhanced cotton's competitive position in the textile industry during the past several years. The accepted chemical modifications are usually reactions occurring at the hydroxyl groups of the anhydroglucose monomer units of the cotton cellulose. Chemical reactions at cellulosic hydroxyl groups are those of any polyhydric alcohol and may be classified as etherifications, esterifications, replacements, and additions. Certain chemical reagents are unable to penetrate the crystalline lattice of cotton cellulose and are therefore unable to react with hydroxyl groups in this region. Other reagents are prevented from reacting with hydroxyl groups in the cellulosic amorphous regions due to a network of hydrogen bonding. In order to achieve a significant chemical modification, it is necessary to increase the availability of the cellulosic hydroxyl groups in both amorphous and crystalline regions. Such increased availability is generally accomplished by pretreatments which cause the cellulose structure to swell. It has been demonstrated that the degree of cotton cellulose swelling is an important factor in the mechanical properties of chemically treated cotton, particularly as regards wet and dry crease resistance resulting from crosslinking treatments (2, 23).[1]

Due to the hydrophilic nature of cellulose, aqueous systems are the most efficient swelling agents and, while water alone causes a marked swelling of cotton fibers, it is possible to increase such swelling by use of acids, bases, and salts (3). The use of aqueous solutions as pretreating swelling systems is a widely accepted technique in the cotton chemical finishing industry, and many reactions of cotton cellulose have been made possible by such swelling pretreatments.

Several reactions of cotton cellulose may be envisaged which can not be conducted in the presence of water. In most of those reactions the active reagent is either unstable to water or would follow an anomalous course of reaction in the presence of water. Non-aqueous swelling agents have been investigated and in general found to swell cellulose less than aqueous systems (22). Both the polarity and molar volume of organic liquids have been found to be important parameters in the degree of cellulose fiber swelling. While the more common organic liquids such as chloroform, carbon tetrachloride, ether, benzene, certain phenyl derivatives, and alcohols have been studied in conjunction with their swelling power, several of these and other classes of organic liquids need to be more thoroughly considered. In the course of this investigation a wide variety of organic liquids were studied in relation to their cotton cellulose swelling power by a number of techniques. The premise was made that the desirable results of a swelling pretreatment are either enhanced reactivity of the cotton cellulose or altered mechanical properties of the cotton fiber, and that the increase in volume of the fiber due to swelling is of importance only to the extent that it is related to changes in fiber chemical and physical properties. In line with this premise, a great deal of attention was given to a study of the pretreated or preswollen fiber. The extent of swelling was evaluated primarily by the imbibition technique, discussed in Chapter II, and by a method involving direct dimensional measurements which is discussed in Chapter III. The pretreated or preswollen fibers were studied by several methods: chemical reactivity, discussed in Chapter VI; differential dyeing, discussed in Chapter IV; and measurements of fiber and yarn mechanical properties, discussed in Chapter VII. An approach to increasing the accessibility or reactivity of cotton cellulose via derivative formation followed by removal

[1] Underscored figures in parentheses refer to Literature Cited at end of report.

of the derivative was attempted and is discussed in Chapter V. In the final chapter the significance of the experimental observations are discussed, conclusions are drawn and recommendations are made. As will be noted in the body of this report, both single and binary organic liquids have been investigated; however these two classes of liquids are not treated separately. The single component organic liquids are considered as the logical extremes of the concentration ranges for the binary systems.

Except as otherwise designated, an experimental cotton which was available from other research programs in these laboratories was used for these studies. The cotton is an experimental strain of Hopi Acala which was grown in Brawley, California. In the course of previous research programs (14), this particular cotton was thoroughly investigated in regard to mechanical properties and structural characteristics. Some of these properties are summarized in Table I-A. The raw cotton was subjected to a Soxhlet extraction procedure with chloroform in order to remove oils and waxes, but no other chemical purification procedure was employed.

TABLE I-A. General properties of the experimental cotton

Micronaire fineness	4.7 μg/in
Array method fineness	4.0 μg/in
Array method mean length	1.02 inches
Maturity	90%
Equilibrium moisture regain	6.36%
Loss in weight in acid hydrolysis	12.1%
X-ray angle	26.3°

CHAPTER II. IMBIBITION STUDIES

GENERAL CONSIDERATIONS

The retention of a liquid by a solid substrate is a ready measure of the ability of the liquid to swell the material under study. While such retention values do not measure true thermodynamic swelling, i. e., volume changes, useful information can be obtained about the relative abilities of a series of liquids to penetrate and swell a polymeric substrate. A measurement of imbibition involves the exposure of the solid polymer to the liquid for a period of time necessary to achieve equilibrium, and the subsequent estimation of the amount of liquid so absorbed. A most convenient means of estimating the amount of liquid absorbed by the polymer is a direct measurement of the increase in weight of the polymer after exposure. The major difficulty in such a direct measurement involves the removal of externally held liquid. The liquid which is held by the polymer externally is generally considered to reside in capillaries which are either formed between fibers or which exist within an individual fiber. The relative ease of removal of this externally held liquid is dependent upon the mean diameter of the capillaries, the distribution of such diameters, and the surface tension of the liquid investigated. Preston and Nimkar (11) have discussed capillary phenomena in assemblies of fibers.

In the present study use was made of the centrifugal method of removing externally held liquid. This technique was discussed by Preston and Nimkar (12) who investigated water retention by various fibers and who have shown that lower retentions are achieved with liquids of lower surface tensions. The surface tension of the water was systematically decreased by the use of wetting agents. In the case of organic liquids the difficulties of removing externally held liquid are less acute since the surface tensions of these liquids are much lower than that of water. Some typical values of surface tension for several organic liquids are shown in Table II-A below.

TABLE II-A. Surface tension at 20°C.

Compound	Surface tension (dynes/cm)
Water	73.0
Methanol	22.6
Ethanol	22.3
Acetone	23.3
Cyclohexanol	33.9
Cyclohexanone	34.5
Benzene	28.9
Chloroform	27.3
Formic acid	37.6
Acetic acid	27.4

It is evident from these values of the surface tension that removal of externally held liquid is much more readily accomplished for organic liquids than for aqueous systems. Thus, imbibition values for organic liquids are probably much more reliable indices of swelling power than similar values for aqueous systems. The centrifuge method for removing externally held liquid has been discussed by many other workers, notably Welo, Ziifle, and McDonald (27), who have investigated the effects of such variables as time and speed of centrifugation and the orientation of the fibers in the bulk sample. Valko and Barnett[1] have applied this technique to a study of the swelling of hair in both aqueous and nonaqueous solvents. Since this study was intended to investigate a wide variety of nonaqueous systems (both single and multicomponent), it was necessary that a relatively rapid method for the measurement of swelling power be available. Despite the many drawbacks of the imbibition method utilizing centrifugal force for removal of externally held liquid, it was decided to use this technique as a rapid screening method. Other techniques of swelling evaluation were used for those organic systems which appeared promising.

1/ Valko, E. I., and Barnett, G., unpublished Masters Thesis. Polytechnic Institute of Brooklyn, June 1952

It should not, however, be considered that the imbibition technique did not yield reliable quantitative data. As will be evident from the data to be presented, much significant information was obtained from the imbibition measurement.

THE METHOD

Basically the method involves the exposure of a previously weighed specimen to the liquid under investigation, removal of externally held liquid by centrifugation, and assessing the liquid which is retained by a simple and direct weight measurement. In this chapter, reference will be made to "water of imbibition" and to "liquid of imbibition." The water of imbibition refers to the water imbibed by a specimen which may or may not have been pretreated by a particular nonaqueous swelling system. Thus, the water of imbibition before and after a given treatment can be used to assess the extent to which the particular pretreatment has disrupted the cellulose structure or the extent to which the nonaqueous system has permanently swollen the cellulose. The liquid of imbibition refers to the amount of liquid retained by the specimen under the conditions of the imbibition test, in which case the liquid is the system whose swelling power toward cellulose is under investigation.

During the course of this work several modifications were made in the technique, but the following general procedure was used: 100-mg specimens of cotton were allowed to soak in the system (or water) under study for one hour. The thoroughly soaked specimen was then placed in centrifuge tubes equipped with false perforated bottoms and subjected to the centrifugal force (G = 232 g) for an initial time period of 30 seconds. The false perforated bottoms are intended to allow removal of the excess liquid and to prevent contact between the specimen and the excess liquid. Evaporation of the liquid was minimized by covering the centrifuge tube with aluminum foil. After centrifugation the specimen was rapidly transferred to an analytical balance and a direct weight was obtained. The specimen was then returned to the centrifuge tube and subjected to further centrifugal force for another increment of time and the weighing step was repeated. The liquid of imbibition values represent the increase in the air dried specimen weight (in percent) after removal of the externally held liquid. In general, weighings were performed after centrifugations of 1/2, 1, 2, 3, 4, 5, 10, 15, 20, and 25 minutes. In Figure 1 are shown some typical curves indicating the amount of liquid retained as a function of the centrifugation time.

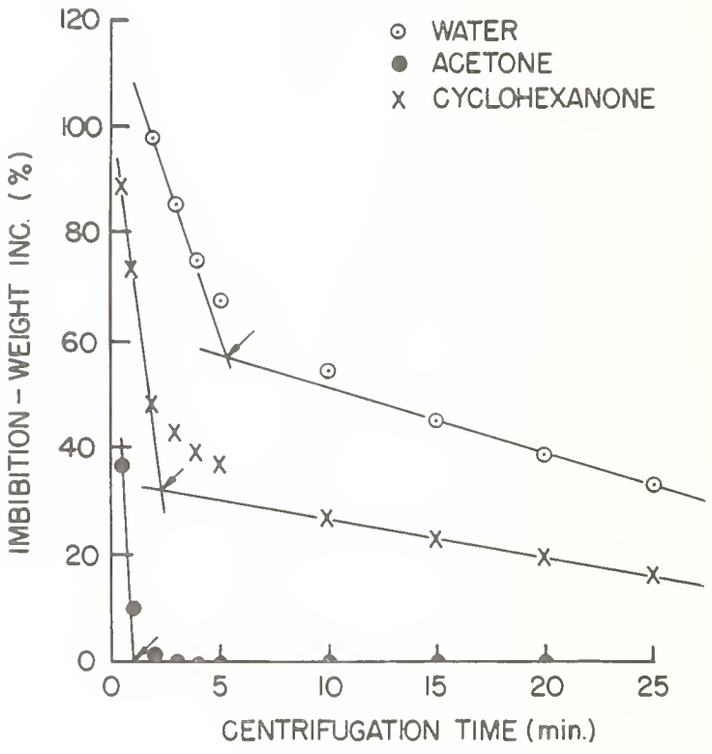

Figure 1. Imbibition weight increase as function of centrifugation time.

It is readily apparent from a consideration of the curves in this figure that most of the externally held liquid is removed within the first five minutes of centrifugation. The major problem is the characterization of the imbibition vs time curve, and several alternatives are possible. One may take as the imbibition value the weight increase after a

certain time of centrifugation, once it has been established that this time of centrifugation places one on a portion of the curve after the rapid loss of externally held liquid. Alternatively the imbibition value may be taken from a consideration of each curve in Figure 1 as being representative of two linear processes. The first process represents the rapid loss of externally held liquid, and the second process represents the loss of liquid which is more tenaciously held or imbibed by the fiber. In many cases the second process does not occur and the latter portion of the weight increase vs time curve is essentially parallel to the x-axis. Lines are drawn through the experimental points to represent the two processes and the ordinate of the intersection point (marked by arrow in Figure 1) is taken as the liquid of imbibition.

Although in this study both methods of imbibition data evaluation were used, the data for and within each system are self-consistent and comparable, but comparison of imbibition values among systems may lead to erroneous conclusions. Each imbibition datum is the mean of four determinations. In all cases the soaking time of the specimen in the liquid was one hour. It will be shown later that no significant effect on imbibition was observed by increasing the soaking time to 16 hours.

EFFECTS OF COTTON MATURITY AND AQUEOUS PRETREATMENTS

It was of interest to determine the effect of cotton fiber maturity on the water of imbibition as well as to determine the effect of several aqueous pretreatments on the water of imbibition values. The aqueous pretreatments were chosen on the basis of their known ability to swell cotton cellulose - mercerization (8) and a treatment in 10 M urea (13). Cotton fiber maturity, while not a direct measure of cellulose structure, has been shown to be related to crystallinity (17).

In an initial series of experiments three different cottons of varying maturity were given the following pretreatments after the standard bulk chloroform extraction process:

a. 10 M urea treatment
b. Mercerization - air drying from water
c. Mercerization - drying by solvent replacement

The urea treatment involved the exposure of a cotton sample to an aqueous 10 M urea solution for 30 minutes at 25° C, washing thoroughly with water and allowing the sample to dry. Both mercerizations involved the treatment in 20% (by weight) NaOH under slack conditions at room temperature for 5 minutes, washing, souring in 1% acetic acid and washing again with water. In one mercerization the sample is allowed to air dry directly from the final water wash; in the other mercerization the final wash water is replaced by acetone which in turn is replaced by diethyl ether, and the sample is finally allowed to air dry from the ether. It was observed that the substitution of methyl alcohol for acetone had no measurable effect on the results. Water of imbibition values were determined for these samples and untreated controls. The results of these experiments are shown in Table II-B below.

TABLE II-B. Water of imbibition (%) for three cottons after several pretreatments

	Cotton No. 41 Maturity = 78	Cotton No. 49 Maturity = 84	Cotton No. 5 Maturity = 90
Control	47.8	43.8	38.4
10 M urea	57.2	59.3	48.8
Mercerized (air dry)	62.0	67.4	57.0
Mercerized (Solvent dry)	69.4	72.0	67.8

Several interesting observations may be made. Significant differences among the three cottons exist as can be seen from the values under control. These values indicate higher imbibition values for cottons of lower maturity, which is in keeping with previous observations that less mature cottons are less crystalline. The 10 M urea treatment and the mercerization treatments significantly increase the water of imbibition values for all three cottons. This indicates the swelling nature of both these treatments. Considering the two mercerization treatments, it is apparent that the solvent drying technique yields a more swollen and presumably a more reactive structure than the air drying technique.

In order to examine the effects of the pretreatments, an imbibition ratio was calculated and defined as the ratio of the water of imbibition value after a given treatment to the imbibition value of the control sample. These values are shown in Table II-C.

TABLE II-C. Imbibition ratios for the three cottons

	Cotton No. 41 Maturity = 78	Cotton No. 49 Maturity = 84	Cotton No. 5 Maturity = 90
10 M urea	1.20	1.35	1.27
Mercerized (air dry)	1.30	1.54	1.48
Mercerized (solvent dry)	1.45	1.64	1.76

Examination of this table clearly reveals the relative effects of the pretreatments on the water of imbibition. The fact that cottons of higher maturity exhibit a greater increase in water of imbibition values than do cottons of lower maturity is suggested by these data. Unfortunately the range of maturity values is too narrow to allow a definite conclusion along these lines. It is clearly evident from these data that the organic solvent replacement technique as a means of drying cotton after mercerization represents a potentially interesting and significant method for increasing reactivity. It is suggested that a thorough investigation of this technique be undertaken with the following specific objective: The elucidation of the effects of solvent drying after mercerization on reactivity, dyeing properties, luster, and mechanical properties relative to the effects of these characteristics of the standard mercerization process. Some observations on the reactivity of cotton mercerized by these two techniques are shown in Chapter VI.

In connection with these experiments on aqueous pretreatments, some interesting observations were made on samples of decrystallized cotton (19, 20). Two samples of decrystallized Deltapine raw stock cotton were obtained through the courtesy of the Southern Regional Research Laboratory with the following information:

SRRL 1 - Residual crystals of cellulose III, 25-40% (est.) crystallinity, pilot plant runs No. 16; treated with monoethylamine for 4 hours and vacuum dried.

SRRL 2 - Residual crystals of cellulose I, 25-40% (est.) crystallinity, pilot plant runs No. 17 and 18; treated with monoethylamine for 4 hours and washed with cold water.

These samples were subjected to the three chemical treatments described above (urea and two mercerizations) and the water of imbibition was measured. Imbibition ratios were calculated (as defined earlier) and the results are presented in bar graph form in

Figure 2. The data for cotton No. 5, which was used in later experiments, is included for comparison purposes in Figure 2.

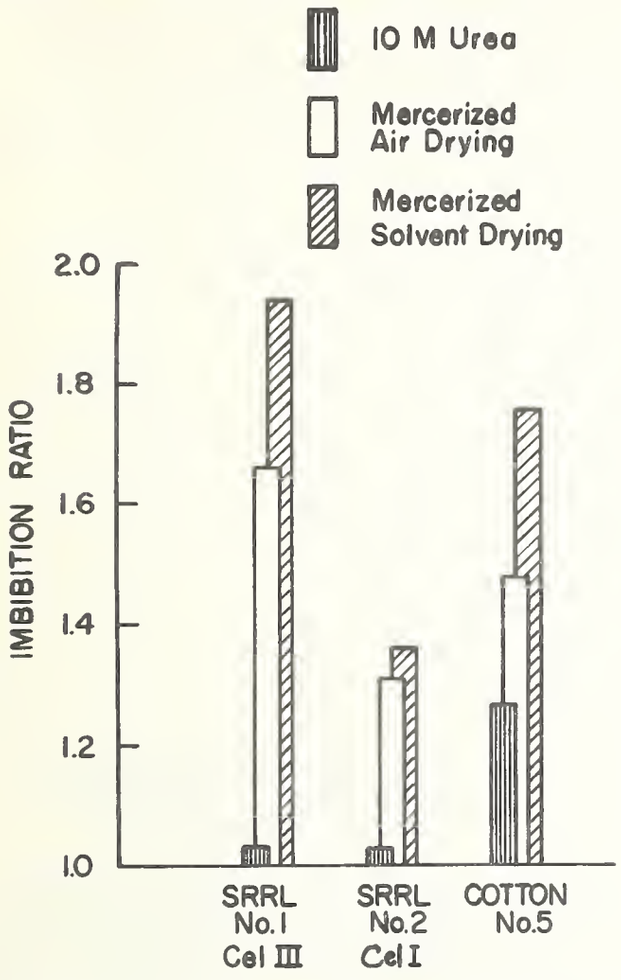

Figure 2. Bar charts showing imbibition ratios for variously pretreated cottons.

It is interesting to note that there is virtually no effect of the 10 M urea treatment on the two decrystallized cottons and that the effects of the two mercerization treatments are different for these two samples. While these experiments are certainly not exhaustive, they suggest an interesting difference in the response to mercerization of cellulose I and cellulose III.

IMBIBITION OF GLYCEROL AND GLYCOL-CONTAINING SYSTEMS

In view of the known hydrophillic nature of glycerol and ethylene glycol (subsequently referred to as glycol), these substances were studied by the imbibition technique as solutes in several representative organic solvents. Aqueous solutions were used for comparison purposes. Wellisch, Hagan, Marker and Sweeting (25, 26) have discussed the interaction between cellulose and glycol, glycerol, and other small molecules by means of equilibrium vapor pressure measurements of cellulose films containing known quantities of such small molecules. In this investigation liquid of imbibition measurements were made for the following solvents: water, ethanol, acetic acid, acetone, and ethyl acetate; and for 10% (by weight) solutions of glycerol and glycol in these solvents. The results of these experiments are shown in Table II-D.

TABLE II-D. Liquid of imbibition (%) for several pure solvents and for 10% solutions of glycerol and glycol in these solvents

Solvent	Solute		
	None	Glycerol	Glycol
Water	33.1	47.4	39.0
Ethanol	0.2	8.6	7.1
Acetic acid	10.7	19.7	14.8
Acetone	0	3.0	2.0
Ethyl acetate	0.1	----	44.5

Considering the pure solvents, it is evident that water is imbibed to the greatest extent with glacial acetic exhibiting a small yet significant imbibition. Acetone, ethanol and ethyl acetate are not imbibed by cotton cellulose to a measurable extent. Glycerol and glycol, at a concentration of 10%, markedly increase the imbibition values, which is particularly true for the nonaqueous systems where the pure solvents are imbibed to a lesser extent. It was of interest to examine the imbibition over the entire concentration range of the glycerol and glycol in the several solvents. In Figure 3 are shown the imbibition values for the ethylene glycol systems where a significant dependence upon concentration is observed in the case of the four solvents studies. The fact that these relationships are nonlinear tends to indicate "compound" formation between solute and solvent where such "compounds" appear to

have characteristic cellulose swelling power.

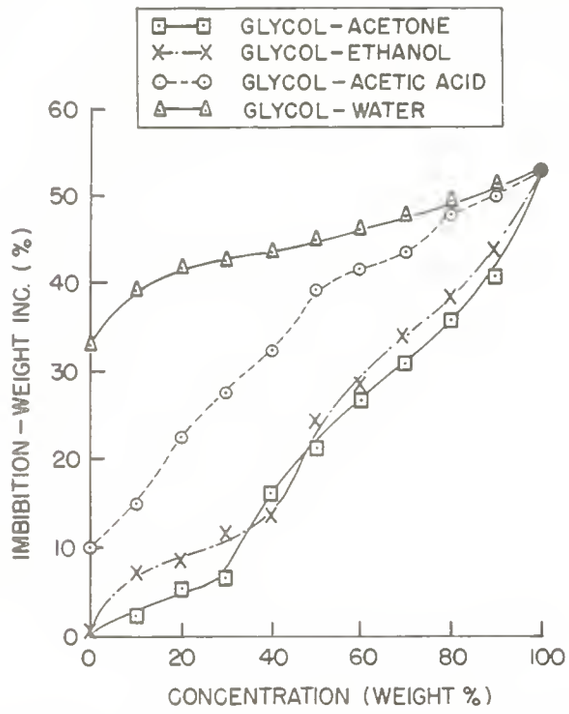

Figure 3. Relationship between liquid of imbibition and concentration of ethylene glycol in various solvents.

Similar relationships are shown for glycerol-solvent systems in Figure 4.

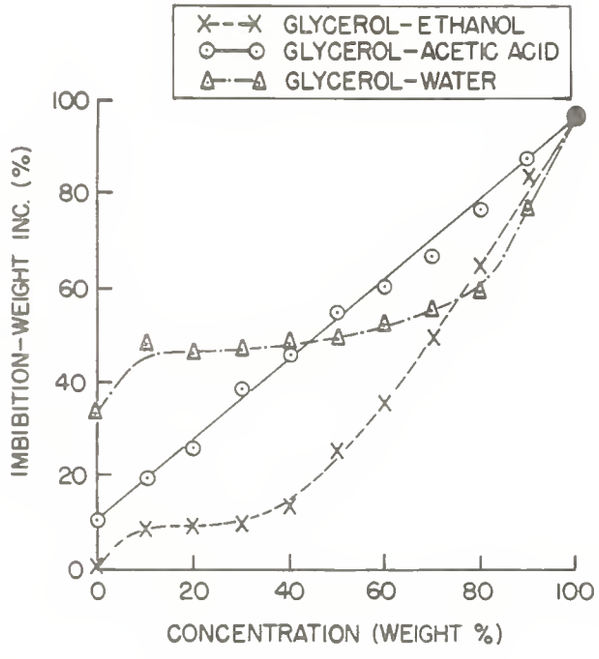

Figure 4. Relationship between liquid of imbibition and concentration of glycerol in various solvents.

In addition to the use of acetic acid as a solvent, two other aliphatic acids were investigated. Glycerol and glycol were used as solutes in formic acid and in propionic acid, and imbibition studies were made over the entire concentration range. The data for the glycol systems are shown in Figure 5 where the data for acetic acid are

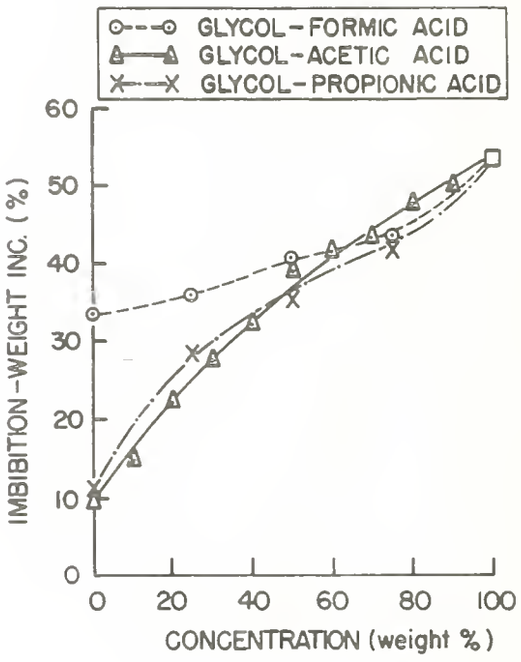

Figure 5. Liquid of imbibition as a function of glycol concentration in three aliphatic acids.

shown again for comparison purposes. A significant effect of glycol concentration on the imbibition value is clearly evident for all three aliphatic acids. At low glycol concentrations formic acid exhibits significantly greater imbibition than either acetic or propionic acids. This unique behavior of formic acid may be ascribed to a chemical esterification reaction between the acid and cellulose, which will be discussed in detail in Chapter V. At higher glycol concentrations, no difference is observed among the three acids. Similar results were obtained using glycerol instead of glycol. It is clear from these results that glycerol and glycol in the nonaqueous solvents, as well as in water, have the ability to swell and be imbibed by cotton cellulose. This behavior is undoubtedly related to the hydrogen bond-forming

characteristics of these solutes. Whether these systems have the ability to penetrate crystalline regions or whether these systems penetrate only the amorphous regions cannot be determined from these results.

It was mentioned previously that experiments were conducted which indicated that the one-hour soaking time was sufficient to achieve equilibrium and that only minor effects were observed by increasing the soaking time to 16 hours. The effect of soaking time was evaluated on the systems: glycerol-water, glycerol-ethanol, and glycerol-acetic acid. The data are summarized in Table II-E. Other experiments on non-aqueous systems containing glycerol and glycol are discussed in Chapters III and IV.

TABLE II-E. Effect of soaking time on liquid of imbibition measurements

Glycerol: H_2O	0/100	25/75	50/50	75/25	100/0
1 hr. soak	33.1	46.0	49.0	58.0	96.5
16 hr. soak	36.4	46.1	49.3	57.9	98.3
Glycerol: AcOH	0/100	25/75	50/50	75/25	100/0
1 hr. soak	10.7	32.0	54.5	75.0	96.5
16 hr. soak	11.1	40.6	57.4	79.6	98.3
Glycerol: EtOH	0/100	25/75	50/50	75/25	100/0
1 hr. soak	0.2	9.0	25.0	58.0	96.5
16 hr. soak	1.6	11.5	26.4	56.6	98.3

IMBIBITION STUDIES OF THE DIMETHYL SULFATE–TOLUENE SYSTEM

As will be discussed in detail in Chapter VI, the dimethyl sulfate-toluene system is of considerable interest as a system capable of both swelling and reacting with cotton cellulose. In this chapter, consideration will be given to imbibition characteristics only. Initially, samples of cotton were allowed to soak for one hour in 100% dimethyl sulfate, 50% toluene-50% dimethyl sulfate, and in 100% toluene. The imbibition, as weight increase, was measured as a function of centrifugation time and the data are displayed graphically in Figure 6. It is readily evident that toluene is not imbibed, that dimethyl sulfate is imbibed to a considerable extent, and that the dimethyl sulfate-toluene mixture is intermediate. It is interesting to note from the data in Figure 6 that a centrifugation time of approximately 10 minutes is sufficient to remove externally held liquid in the case of toluene and the toluene-dimethyl sulfate mixture, but that the amount of pure dimethyl sulfate continues to decrease, although slowly, as centrifugation time is increased

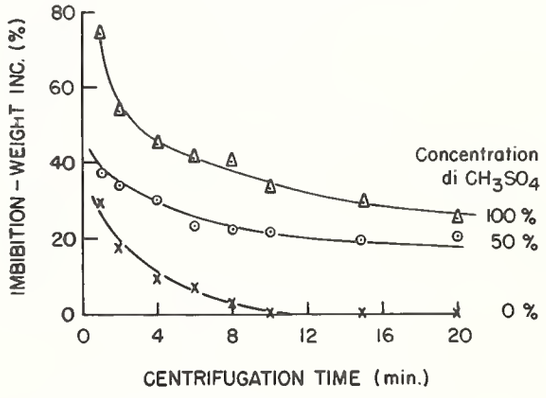

Figure 6. Imbibition of the dimethyl sulfate-toluene system as function of centrifugation time.

beyond 10 minutes. The entire range of dimethyl sulfate concentrations in toluene were studied and the liquid of imbibition as a function of dimethyl sulfate concentration is plotted in Figure 7. The strong dependence of imbibition upon dimethyl sulfate concentration clearly indicates the swelling power of this reagent toward cotton cellulose. The potentialities of this and other reactive systems are discussed in Chapter VI.

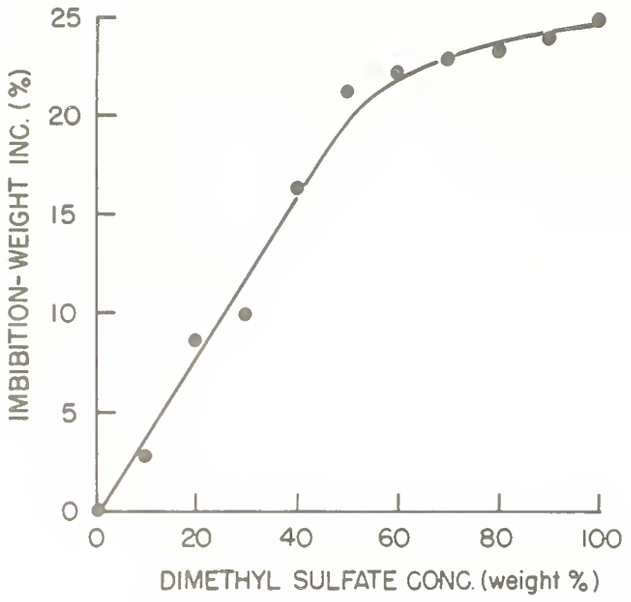

Figure 7. Imbibition as function of dimethyl sulfate concentration in toluene. Centrifugation time: 20 minutes.

SOLUTIONS OF CITRIC ACID, TARTARIC ACID, AND UREA

The significant effects of both glycerol and glycol on imbibition of a variety of organic solvents were ascribed to the ability of these two compounds to disrupt hydrogen bonds and to their ability to satisfy the hydrogen bonding power of cellulose. It was thought desirable, therefore, to investigate the effects of other solutes which may exhibit such properties to a greater extent. Citric acid, tartaric acid and urea were chosen as potentially useful reagents for this purpose on the basis of their organo-chemical structure and properties. That an effect of these solutes was to be expected is evident from the previously discussed effects of an aqueous 10 M urea solution on the water of imbibition. The data in Table II-F on the liquid of imbibition of a series of aqueous citric acid and urea solutions are also pertinent. Solutions of the three solutes (citric acid, tartaric acid, and urea) were prepared in acetone and ethanol. The effects of these solutes in cyclohexanone and cyclohexanol will be discussed in the next section. It was not possible to prepare solutions in acetone and ethanol over a wide concentration range, but wherever solubility properties permitted, solutions up to 20% (by weight) were prepared. The data are presented in Tables II-G and II-H.

TABLE II-F. Liquid of imbibition (%) of aqueous solutions of urea and citric acid

Concentration (weight %)	Urea	Citric Acid
0	33.1	33.1
10	37.9	39.0
20	44.6	41.9
30	53.5	45.2
40	58.6	49.4
50	63.3	59.1

TABLE II-G. Effects of solutes in ethanol on liquid of imbibition (%)

Concentration (weight %)	Citric acid	Tartaric acid	Urea
0	0	0	0
2	0.1	0.8	0
5	----	----	2.3
10	11.9	10.1	---
20	23.3	16.2	---

TABLE II-H. Effects of solutes in acetone on liquid of imbibition (%)

Concentration (weight %)	Citric acid	Tartaric acid	Urea
0	0	0	0
0.5	----	----	0.2
2	1.2	2.1	---
10	6.6	----	---
20	21.2	----	---

The addition of citric acid or tartaric acid to acetone and ethanol clearly increases the swelling power relative to the pure solvents. Urea is almost completely insoluble in these solvents at room temperature and thus could not be studied over as wide a concentration range as were the other solutes. It is evident that these solutes are effective although not to the same extent as glycerol or glycol. A point of considerable interest centers around the question whether

a preferential absorption of one of the components of a binary system takes place. It is conceivable that the liquid is not imbibed in the same composition or, in other words, that there is a preferential absorption of one specie. It is suggested therefore that a study be undertaken of the absorption of selected solutes from nonaqueous solutions.

EFFECTS OF CYCLIC SOLVENTS

Sprague, Riley, and Noether (21) have shown that cyclohexanone is a good swelling agent for cellulose triacetate, and it was of interest therefore to examine its effect on native cotton cellulose. Solutions of cyclohexanone and cyclohexanol in ethanol, acetone, formic acid, acetic acid, and propionic acid were studied over the full range of concentrations. Samples of bulk cotton were treated for one hour at room temperature and the liquid of imbibition was measured. The data are shown in Tables II-I and II-J and are also presented graphically in Figures 8 and 9.

TABLE II-I. Liquid of imbibition-weight increase (%) Cyclohexanone systems

	Cyclohexanone concentration (weight %)				
	0	25	50	75	100
Ethanol	0	11.8	19.5	28.0	32.1
Acetone	0	11.4	20.2	29.5	32.1
Formic acid	45.7	55.0	44.8	32.0	32.1
Acetic acid	8.3	29.5	30.8	33.8	32.1
Propionic acid	25.2	34.4	35.0	33.4	32.1

TABLE II-J. Liquid of imbibition-weight increase (%) Cyclohexanol systems

	Cyclohexanol concentration (weight %)				
	0	25	50	75	100
Ethanol	0	16.1	39.6	47.2	63.1
Acetone	0	15.3	34.8	59.7	63.1
Formic acid	45.7	44.0	40.0	48.2	63.1
Acetic acid	8.3	35.1	42.8	52.0	63.1
Propionic acid	25.2	36.2	45.5	52.2	63.1

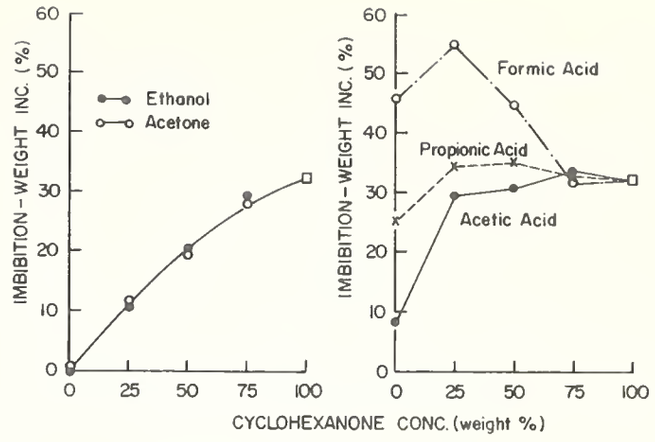

Figure 8. Imbibition as function of cyclohexanone concentration in several solvents.

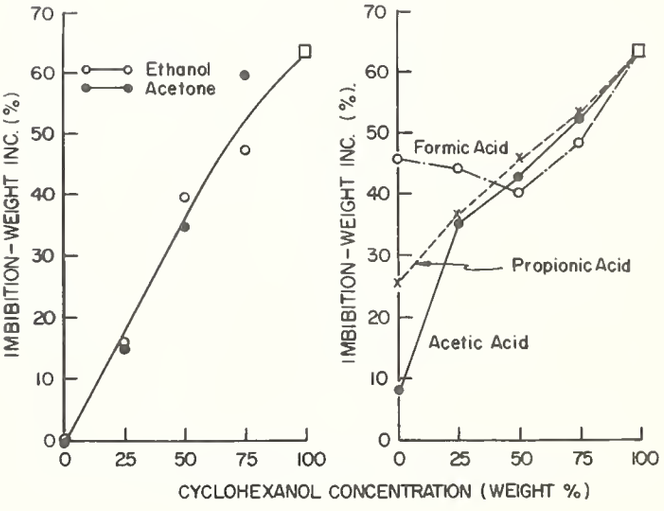

Figure 9. Imbibition as function of cyclohexanol concentration in several solvents.

It is evident from these data that both cyclohexanone and cyclohexanol penetrate and presumably interact with the cellulose and that they are retained under the conditions of the imbibition test. When either acetone or ethanol are used as solvent, the dependence of the retention on concentration of the cyclic compound is essentially linear while, when cyclohexanone is used with these two aliphatic acids as solvent, no further increase in retention is observed above 25%

cyclohexanone. The formic acid system is a special case in view of its previously indicated reactivity toward cellulose, and a minimum in retention is observed with cyclohexanol, while a maximum is suggested with cyclohexanone.

Since both cyclohexanol and cyclohexanone appear to be absorbed by cotton cellulose, it became of interest to determine the effect of various solutes on these reagents. The solutes were the ones considered previously, namely, citric acid, tartaric acid, urea, and glycerol. Unfortunately only a limited range of concentrations could be achieved. The treatments in these binary systems were the usual one-hour soaking followed by an imbibition measurement. The data are presented in Tables II-K and II-L.

TABLE II-K. Effects of solutes in cyclohexanone on liquid of imbibition (%)

Concentration (weight %)	Citric acid	Tartaric acid	Urea	Glycerol
0	32.1	32.1	32.1	32.1
0.1	----	----	36.1	----
2.0	37.2	45.5	----	33.8
10.0	50.0	----	----	----

TABLE II-L. Effects of solutes in cyclohexanol on liquid of imbibition (%)

Concentration (weight %)	Citric acid	Tartaric acid	Urea	Glycerol
0	63.1	63.1	63.1	63.1
1.0	----	----	73.8	----
2.0	72.0	74.0	----	59.2
10.0	69.0	----	----	63.0

The data in these tables suggest that the solutes in general increased the imbibition of cyclohexanone and cyclohexanol; however, it is also evident that the effects of these solutes were not as pronounced on the ability of cyclic solvents to be imbibed as they were on the solvents studied previously (ethanol, acetone, aliphatic acids, etc.). The implications of these significant results which suggest the importance of molecular shape and configuration will be discussed in Chapter VIII. The effects of treatments in systems containing cyclohexanol and cyclohexanone on differential dyeing properties are discussed in Chapter IV.

SUCCESSIVE SYSTEMS

Studies were conducted to determine the effectiveness of certain nonaqueous systems in a successive treatment sequence. Basically, it was desired to introduce an organic reagent into the cellulose matrix which had been preswollen with a given system. Thus, for example, experiments were conducted to determine whether acetone could be introduced into cotton cellulose which was preswollen with a 10% solution of citric acid in cyclohexanone. Further, it was desired to determine whether cotton cellulose imbibition of water could be increased by one or two pretreatments in organic systems. The experimental procedure involved soaking a cotton sample in reagent I for one hour at room temperature, centrifuging for 25 minutes, and recording the weight increase. This pretreated sample was then introduced into either acetone or ethanol (two fresh portions), centrifuged for 25 minutes, and the increase in weight recorded. After the acetone or ethanol treatment, the sample was introduced into two portions of water, and the water of imbibition was measured in the usual manner. The several combinations which were studied and the results obtained are shown in Tables II-M and II-N.

In general, the results must be considered highly disappointing since no measurable quantities of either acetone or ethanol could be incorporated in cotton cellulose which had been preswollen in most of the single component and binary systems listed as reagent I in the tables of data. Only in the cases where reagent I contained formic acid was a significant quantity of acetone or ethanol retained. This unique effect of formic acid may be attributed to the ability

of this acid to react with cellulose. Citric acid in cyclohexanone appears to exert a positive effect on subsequent acetone retention, but a similar effect in the corresponding cyclohexanol-ethanol system was not observed. It will be noted that only minor increases in the water of imbibition were achieved as a result of the successive organic pretreatment sequences. Two percent glycerol in either cyclohexanol or cyclohexanone and the 10% citric acid in cyclohexanone are the most effective in this regard, although even these effects must be considered minor.

TABLE II-M. Successive nonaqueous systems. Cyclohexanone-acetone-water series

Reagent I	25 Min. imbibition-weight increase (%)		
	Reagent I	Acetone	Water
-----	none	none	31.7
-----	none	0.7	35.1
Cyclohexanone	19.3	none	33.0
Cyclohexanone	16.6	0	35.5
10% Citric acid in cyclohexanone	23.7	2.3	37.8
2% Tartaric acid in cyclohexanone	19.1	0	32.4
2% Glycerol in cyclohexanone	17.3	0	37.5
50% Formic acid in cyclohexanone	25.5	3.1	30.2
50% Acetic acid in cyclohexanone	13.7	0	33.0
50% Propionic acid in cyclohexanone	15.8	0	33.3

TABLE II-N. Successive nonaqueous systems. Cyclohexanol-ethanol-water series

Reagent I	25 Min. imbibition-weight increase (%)		
	Reagent I	Ethanol	Water
-----	none	none	31.7
-----	none	0.6	38.8
Cyclohexanol	56.1	none	37.7
Cyclohexanol	58.2	0	32.6
10% Citric acid in cyclohexanol	70.0	0.8	30.2
2% Tartaric acid in cyclohexanol	52.8	0.3	34.0
2% Glycerol in cyclohexanol	47.5	0	37.4
50% Formic acid in cyclohexanol	26.1	3.0	27.3
50% Acetic acid in cyclohexanol	24.2	0	35.2
50% Propionic acid in cyclohexanol	26.0	0	30.7

It should be pointed out that the imbibition values for reagents I in Tables II-M and II-N are frequently different from values for the same reagents shown in some earlier tables. The reason for these discrepancies is the 25-minute centrifugation time which was used in the study of the successive systems. In other studies, shorter centrifugation times and other methods of characterizing the imbibition versus time curves were employed.

IMBIBITION OF GLUCOSEPENTAACETATE SOLUTIONS

The results which have been obtained by the imbibition technique suggest the importance of molecular shape and configuration. It became of interest, therefore, to examine the effects of a solute which might be configurationally favorable for interaction with cotton cellulose. In view of its solubility in organic solvents, glucosepentaacetate was chosen for this purpose. Solutions of this sugar derivative were prepared in acetone, benzene, and chloroform. Only minor and essentially negligible imbibition was observed for these pure solvents. The imbibition properties of the glucosepentaacetate solutions in these solvents were measured and are presented in Table II-O. It is readily evident that the sugar moiety has a pronounced effect on imbibition. It must be concluded that this effect is due to the favorable configuration of glucosepentaacetate since this derivative can have no particular hydrogen bond breaking power. The implications of the data in Table II-O will also be discussed in Chapter VIII.

TABLE II-O. Liquid of imbibition-weight increase (%)

Solvent	Glucose-pentaacetate conc. weight %	Imbibition weight increase (%)
Acetone	0	0
	1	1.6
	2	2.0
	5	2.4
	10	6.2
	20	11.2
Benzene	0	2.4
	1	4.6
	2	3.4
	5	8.5
	10	10.4
Chloro-form	0	1.1
	1	4.0
	2	3.2
	5	5.8
	10	12.7

CHAPTER III. DIMENSIONAL MEASUREMENTS

GENERAL CONSIDERATIONS

Several nonaqueous, single component and binary systems were studied by their effect on the dimensions of cotton fibers and yarns. While such direct measurements are tedious and time-consuming, it was thought possible that significant information might be obtained by this technique. Liquid systems which are able to penetrate the cotton fiber cellulosic matrix should cause an increase in fiber length, as well as an increase in the fiber cross-sectional area. In view of the anisotropic structure of a cotton fiber, the increase in length is considerably less than the increase in cross-sectional area, thus necessitating extremely careful measurements. In view of complex yarn geometry, exposure of a spun yarn to a liquid system which causes fiber swelling should result in a yarn contraction. Thus, for example, in the case of water, single fibers increase in length by about 2% of their original dry length, while yarns contract under similar conditions by about 3% of their original length (5). The dimensional changes of both individual fibers and spun yarns are highly dependent upon the tension which is exerted on the fiber or yarn during the measurement. It is necessary that the restraining force be carefully controlled when different liquid systems are under investigation.

FIBER MEASUREMENTS

Individual cotton fibers were mounted on brass tabs at approximately 1/2 in. gauge spacing. During the swelling measurement the lower tab was allowed to hang freely, thus providing a finite restraining load. The magnitude of this restraining force was controlled by the size of the lower tab. In most cases the restraining load on each fiber was 3 mg (in air), although 50 mg was used in one series of experiments. The length of the fiber is carefully measured with a traveling microscope in air to obtain the original length, l_o. The fiber length is then measured after various times of exposure in the system under study and is designated as l_t at any time t. The change in length or fiber swelling, FS, is computed as follows:

$$FS = \frac{l_t - l_o}{l_o} \cdot 100$$

Two series of systems were evaluated by this technique:

1. Aliphatic alcohols and 50% glycerol solutions in aliphatic alcohols
2. Dimethyl sulfate - toluene

In Table III-A are shown FS values for single fibers exposed to water and a series of aliphatic alcohols at room temperature (≈25° C) and at 50° C. Each value is the mean of at least two single fiber measurements and represents the FS value after a 30 minute exposure to the liquid at which time a near equilibrium had been attained.

TABLE III-A. Change in length (FS values) of single fibers in aliphatic alcohols at room temperature and at 50° C. Fiber tension = 3 mg.

System	Change in fiber length (%)	
	Room temp.	50° C.
Water	2.78	3.54
Methanol	2.51	3.53
Ethanol	-0.02	2.64
i-Propanol	1.04	0.37
n-Butanol	-0.49	1.54
n-Pentanol	-0.92	-0.62

Both at room temperature and at 50° C, methanol appears to be as efficient a swelling agent as water. At room temperature swelling power decreased rapidly for the higher members of this homologous series and, with the exception of isopropanol, negative

FS values were obtained. At 50°C ethanol acted as a swelling agent and only in the case of n-pentanol was a negative FS value observed. The negative values may indicate the ability of the reagent to extract water from the cellulosic matrix. Similar results have been obtained in the case of wood fibers by Stamm and his coworkers (22).

In Table III-B are shown FS values for single fibers exposed to 50% glycerol solutions in the aliphatic alcohols. Pentanol could not be included in view of solubility considerations. Values again represent the means of at least two measurements after 30-minute exposure at room temperature and at 50°C. It is readily apparent that the glycerol-water system was a better swelling agent than water at both temperatures.

TABLE III-B. Change in length (FS values) of single fibers in 50% glycerol - aliphatic alcohol solutions at room temperature and at 50°C. Fiber tension = 3 mg.

System	Change in fiber length (%)	
	Room temp.	50°C.
50% Glycerol in		
water	3.62	5.29
methanol	-0.13	4.71
ethanol	-0.46	2.29
i-propanol	-0.24	0.37
n-butanol	-0.77	-0.66

The introduction of glycerol into the alcohols caused an increase in the FS values only with methanol at the higher temperature. Once again, swelling power decreased for the higher members of the homologous series. The introduction of glycerol into the alcohols at room temperature resulted in greater contraction rather than swelling. This may be associated with the ability of such binary systems to extract water from the fiber. It would be of extreme importance in this connection to perform fiber-swelling measurements on bone dry fibers. No definitive relation between swelling power as measured by this technique and physico-chemical constants of these liquids could be established. The data are summarized in the form of bar charts in Figure 10.

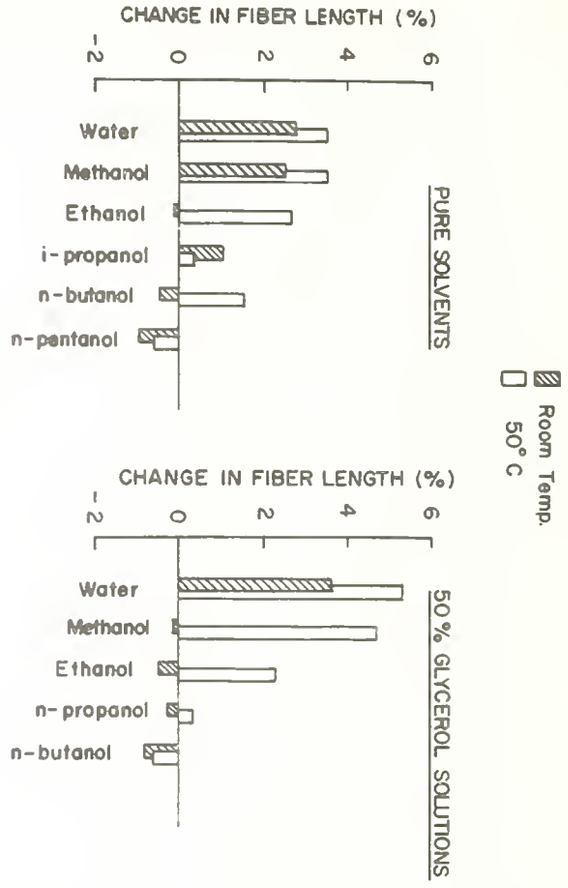

Figure 10. Bar charts showing changes in fiber length (under 3 mg tension) in various alcohols and in 50% glycerol-alcohol solutions at room temperature and at 50°C. Measurements after 30 minutes exposure.

Individual fiber swelling measurements by the change-in-length technique were also performed for the dimethyl sulfate-toluene system. In one series of experiments each fiber was maintained under 3 mg tension; in another series each fiber was maintained under a tension of 50 mg. All experiments were performed at room temperature. Each fiber was first allowed to come to dimensional equilibrium in toluene under the specified tension. This equilibrium was attained in about 10 to 15 minutes (frequently less), after which time specified quantities of dimethyl sulfate were added to the measure-

ment cell. Fiber length was then measured as a function of time, during periods of time shown in Figure 11, where rapid changes in length occurred. It is evident from these curves that addition of dimethyl sulfate caused a marked cotton fiber swelling as measured by the increase in fiber length.

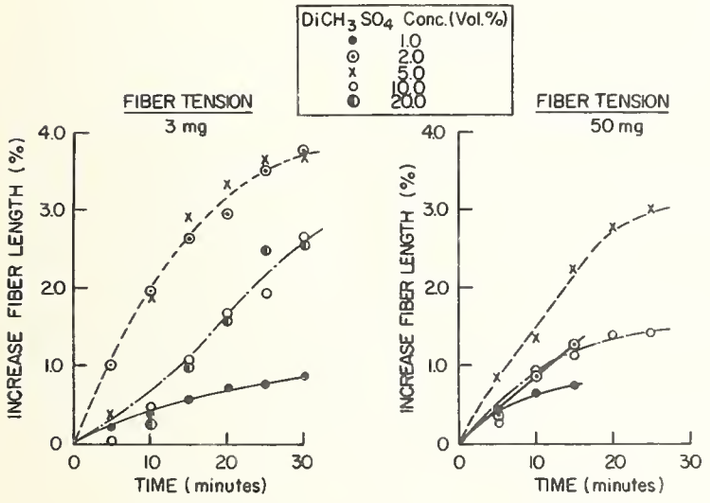

Figure 11. Increase in fiber length as function of time in dimethyl sulfate-toluene systems.

The swelling power is strongly dependent upon the dimethyl sulfate concentration, but not in a continuous manner as might have been anticipated. With the measurements being performed under a 3 mg tension on each fiber, the data clearly group into three relationships as shown in Figure 11. At any time the 1% solution caused least swelling, the 2 and 5% solutions caused most swelling, while the 10 and 20% dimethyl sulfate solutions caused intermediate increases in fiber length. With the fibers under 50 mg tension, the grouping is similar although not identical. However, once again the greatest swelling is caused by the 5% dimethyl sulfate solution. In Figure 12 are shown the FS values after 15-minute exposure of the fibers to the various solutions. The maximum swelling power of solutions of intermediate dimethyl sulfate concentration is clearly evident from these bar charts. The dimethyl sulfate-toluene system is obviously an interesting potential swelling agent for cotton cellulose and deserves further study. Other experiments on the dimethyl sulfate-toluene system are described in Chapter VI.

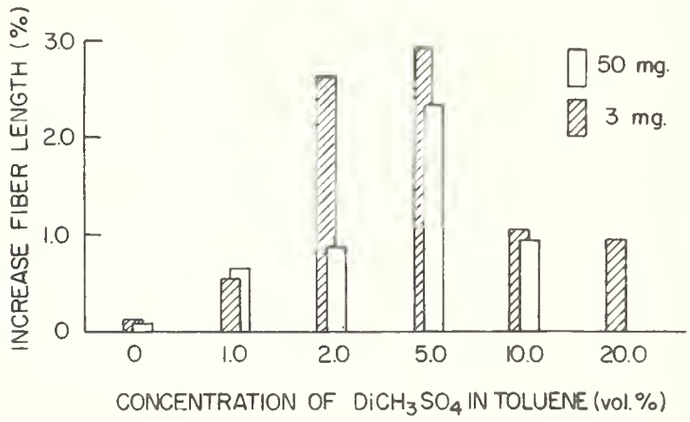

Figure 12. Bar charts showing increases in fiber length in dimethyl sulfate-toluene systems.

YARN MEASUREMENTS

The effects of various nonaqueous single component and binary systems on yarn dimensions were studied. A 40/3 combed Supima cotton yarn was used for these experiments. Specimens were mounted at 5 cm. gage spacing on brass tabs and l_o measured in air under a restraining load of 30 mg. The reagent under investigation was then introduced into the measurement cell and yarn length, l_t measured at various times, t. In the initial experiments l_t was measured in 5-minute intervals between 0 and 60; however, in later experiments l_t was measured at t=30 minutes and t=60 minutes only. Yarn contraction, YC, a direct measure of fiber swelling was computed as follows:

$$YC = \frac{l_o - l_t}{l_o} \quad 100$$

Yarn contraction measurements were performed in the following systems:

1. Aliphatic acids
2. 50% Glycerol in aliphatic acids
3. Several solutes in ethanol, acetone, cyclohexanone and cyclohexanol.

In Table III-C are shown yarn contraction values after 30- and 60-minute exposure to several single component systems at room temperature.

TABLE III-C. Yarn contraction values-single component systems at room temperature. Yarn specimens under 30 mg. tension

System	Yarn contraction (%)	
	30 min.	60 min.
Water	3.28	3.34
Formic acid	3.42	3.48
Acetic acid	0.57	0.64
Propionic acid	0.88	0.92
Ethanol	0.60	0.64
Acetone	0.50	0.52
Cyclohexanol	0.78	0.87
Cyclohexanone	0.59	0.67
Glycerol	1.35	1.44
Chloroform	0.40	0.34

It is apparent that swelling was virtually complete in 30 minutes and that little additional yarn contraction takes place during the latter 30-minute period. It is clearly evident that only formic acid caused a substantial yarn contraction, approximating that caused by water. This fact is due to the reactive nature of formic acid toward cotton cellulose, as discussed in detail in Chapter V. The other aliphatic acids caused some yarn contraction relative to that caused by chloroform, which may be taken to represent a typical nonswelling system. Similarly, ethanol, acetone, cyclohexanone, and cyclohexanol cause some yarn contraction relative to that of chloroform. None of these reagents, however, exhibit the swelling power of either water or formic acid. Glycerol apparently penetrated the cellulosic structure to some extent, causing a fairly large yarn contraction.

Fifty percent solutions of glycerol in water and in the aliphatic acids caused yarn dimensional changes which are particularly interesting when compared to the effects of the pure solvents. The data for these binary systems are presented in Table III-D.

TABLE III-D. Yarn contraction values-binary systems at room temperature. Yarn specimens under 30 mg. tension

System	Yarn contraction (%)	
	30 min.	60 min.
50% Glycerol in water	2.13	2.26
50% Glycerol in formic acid	0.93	1.00
50% Glycerol in acetic acid	1.15	1.25
50% Glycerol in propionic acid	1.37	1.47

and are compared with the pure solvents in bar chart form in Figure 13.

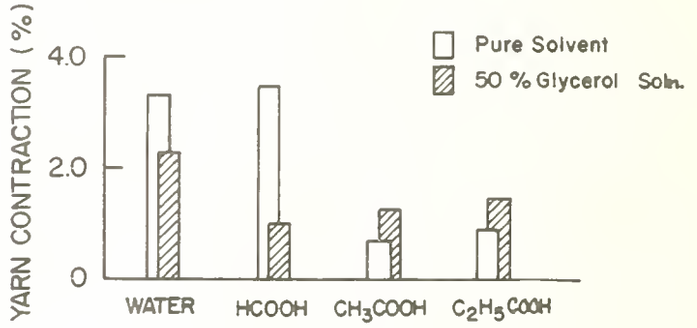

Figure 13. Bar charts showing yarn contractions in aliphatic acid systems.

It is of interest that the introduction of glycerol (50%) into water and formic acid caused a reduction in swelling, whereas the introduction of glycerol into acetic and propionic acid caused an increase in swelling. Thus, glycerol, which is a reagent of intermediate swelling power, increased the swelling power of a poor reagent but decreased the swelling power of a good swelling reagent.

Other binary systems were studied and yarn contraction values are presented in Table III-E. It is apparent that the addition of citric acid, tartaric acid, and glycerol to ethanol, acetone, cyclohexanol, and cyclohexanone did not cause an increase in the swelling power of the solvent as measured by the yarn contraction method.

Attempts to establish correlations between yarn contraction values and other parameters of swelling proved fruitless. For example, although both cyclohexanone and cyclohexanol have high imbibition values their yarn contraction values are not appreciably different from those of acetone and ethanol. Similar lack of correlation exists for the case of water and acetic acid solutions of glycerol. In all probability this lack of correlations must rest with the yarn contraction measurements which are relatively insensitive and difficult to evaluate.

TABLE III-E. Yarn contraction values - binary systems at room temperature. Yarn specimens under 30 mg. tension

System	Yarn contraction (%)	
	30 min.	60 min.
2% Citric acid in		
ethanol	0.85	0.92
acetone	0.40	0.43
cyclohexanol	0.89	0.94
cyclohexanone	0.37	0.43
10% Citric acid in		
ethanol	0.86	0.93
acetone	0.60	0.66
cyclohexanol	0.57	0.69
cyclohexanone	0.68	0.78
2% Tartaric acid in		
ethanol	0.70	0.74
acetone	0.33	0.42
cyclohexanol	0.62	0.74
cyclohexanone	0.12	0.14
2% Glycerol in		
ethanol	0.83	0.91
acetone	0.54	0.58
cyclohexanol	0.75	0.85
cyclohexanone	0.38	0.47

CHAPTER IV DIFFERENTIAL DYEING STUDIES

GENERAL CONSIDERATIONS

Differential dyeing as a means for estimating cotton fiber maturity and structure was first described by Goldthwait and his coworkers (6, 7), and subsequently placed on a quantitative basis by Rebenfeld and Wu (17). In the quantitative adaptation, the dye uptake is measured objectively by a spectrophotometric analysis of the dyes extracted from the sample. G is defined as the dye uptake of the high molecular weight dye (Chlorantine Green BLL), and R is defined as the uptake of the low molecular weight dye (Diphenyl Fast Red 5BL). Both the total dye uptake (G+R) and the ratio G/R have been shown to be sensitive indices of fiber maturity and structure. It has been shown that certain aqueous swelling pretreatments significantly affect the differential dyeing properties, and it has been suggested that swelling may be studied by differential dyeing (17). In this chapter the effects of swelling treatments in a variety of single component and binary systems on the differential dyeing properties of cotton will be discussed.

Unless otherwise specified the swelling treatment consisted of soaking a one-gram cotton sample in 100 ml. of the liquid system under study for one hour at room temperature. After filtration of the sample on a glass filter, the material was washed with three portions of the particular solvent and allowed to air dry overnight. The pretreated cotton was then subjected to the standard quantitative differential dye test as described by Rebenfeld and Wu (17).

GLYCOL AND GLYCEROL SYSTEMS

In Table IV-A are shown dye uptake and G/R values for cotton samples which had been subjected to several treatments. In the case of the ethylene glycol and glycerol swelling systems, cotton samples were immersed in these liquids at room temperature for one hour and, after removal of excess liquid by filtration, the samples were allowed to air dry overnight. The differential dyeing test was then performed directly on these samples. It was determined that during this technique of preswelling, 3.7 grams of glycerol, and 2.5 grams of glycol were retained by 1-gram cotton samples. In order to determine whether the presence of these amounts of reagents in the dye bath had an effect on the differential dyeing, blank dyeings were performed where equivalent quantities of glycol or glycerol were added directly to the dye bath. In addition to the samples treated with glycol or glycerol, the differential dyeing properties of an untreated cotton and a standard mercerized cotton are shown.

TABLE IV-A. Effects of glycerol and glycol treatments on differential dyeing

Swelling system	Dye uptake (mg./gram)			G/R value
	Red	Green	Total	
Untreated	6.9	12.3	19.2	1.77
Mercerized	15.9	35.4	51.3	2.22
Glycerol	6.7	14.6	21.3	2.18
Glycol	6.7	14.8	21.5	2.21
None, but equivalent glycerol added to dye bath	6.4	11.9	18.3	1.85
None, but equivalent glycol added to dye bath	6.8	12.4	19.2	1.82

The standard aqueous mercerization has great effects on the differential dyeing properties which are in keeping with the well known effects of mercerization on dyeing characteristics resulting from changes in the degree of crystallinity. These changes are manifest as a major increase in the total dye uptake as well as an increase in the G/R value. Treatment with either glycol or glycerol has a similar effect although the increase in the total dye uptake is much smaller than in the case of mercerization. It is interesting, however, that the G/R value is essentially equal for the mercerized and for the polyhydric alcohol-treated samples. These facts indicate the necessity of considering changes in both the total dye uptake and the G/R value, and of not relying upon either one or the other of the parameters alone. The mere presence of equivalent quantities of either glycol or

glycerol in the dye bath is not responsible for the altered dyeing properties as is evident from the data in Table IV-A. One must therefore conclude that treatments in either of these polyhydric alcohols alter the dyeing properties and therefore presumably the physico-chemical structure of the cotton cellulose.

In view of the results obtained with pure glycol and glycerol, a variety of binary systems containing these polyhydric alcohols were studied in regard to their effectiveness in altering the differential dyeing properties of cotton celluloses. Solutions were readily prepared at room temperature of glycerol and glycol in three aliphatic acids over the entire composition range. The effects on differential dyeing of treatments in these solutions are shown in Tables IV-B and IV-C.

TABLE IV-B. Effects of swelling cotton in glycerol-aliphatic acid systems on differential dyeing characteristics

Swelling System (weight %)	Dye uptake (mg/gram)			
	Red	Green	Total	G/R value
Formic acid				
0% glycerol	13.4	16.5	29.9	1.22
25% glycerol	14.9	17.0	31.9	1.13
50% glycerol	16.0	17.4	33.4	1.08
75% glycerol	17.3	18.1	35.4	1.04
Acetic acid				
0% glycerol	7.5	13.3	20.8	1.76
25% glycerol	9.0	14.0	23.0	1.54
50% glycerol	10.4	15.2	25.6	1.46
75% glycerol	10.9	15.6	26.5	1.43
Propionic acid				
0% glycerol	8.0	13.6	21.6	1.69
25% glycerol	8.0	13.4	21.4	1.67
50% glycerol	8.3	13.6	21.9	1.63
75% glycerol	9.0	13.6	22.6	1.51
Untreated	6.9	12.3	19.2	1.77
Water	6.8	12.5	19.3	1.84
Mercerized	15.9	35.4	51.3	2.22

TABLE IV-C. Effects of swelling cotton in glycol-aliphatic acid systems on differential dyeing characteristics

Swelling system (weight %)	Dye uptake (mg/gram)			
	Red	Green	Total	G/R value
Formic acid				
0% glycol	13.4	16.5	29.9	1.22
25% glycol	13.3	15.3	28.6	1.15
50% glycol	13.6	14.8	28.4	1.09
75% glycol	14.8	14.2	29.0	0.96
Acetic acid				
0% glycol	7.5	13.3	20.8	1.76
25% glycol	8.9	14.5	23.4	1.64
50% glycol	9.6	15.4	25.0	1.59
75% glycol	10.4	15.8	26.2	1.53
Propionic acid				
0% glycol	8.0	13.6	21.6	1.69
25% glycol	9.4	15.1	24.5	1.61
50% glycol	10.1	15.6	25.7	1.55
75% glycol	11.2	16.8	28.0	1.49
Untreated	6.9	12.3	19.2	1.77
Water	6.8	12.5	19.3	1.84
Mercerized	15.9	35.4	51.3	2.22

Treatments in systems containing formic acid result in an increase in the total dye uptake and a large decrease in the G/R value. As will be discussed in Chapter V, treatments in systems containing formic acid cause a chemical reaction to take place, resulting in a formylated cotton cellulose. Treatments in glycerol-acetic acid, glycerol-propionic acid, glycol-acetic acid, and glycol-propionic acid systems result in a material whose dyeing properties are slightly altered as indicated by an increase in total dye uptake and a decrease in the G/R value. Treatments in the pure aliphatic acid (without the polyhydric alcohol) cause some of the effect. There is a pronounced additional effect upon addition of either glycol or glycerol to either propionic or acetic acid. Clearly these systems represents potential nonaqueous swelling systems for cotton cellulose.

Binary systems composed of either glycol or glycerol and several other organic liquids as well as water have also been investigated in terms of their effect on differential dyeing properties. The data are summarized in Tables IV-D and IV-E.

TABLE IV-D. Effects of swelling cotton in glycol-solvent systems on differential dyeing characteristics

Swelling system (weight %)	Dye uptake (mg/gram)			G/R value
	Red	Green	Total	
Water				
0% glycol	6.8	12.5	19.3	1.84
25% glycol	6.6	11.4	18.0	1.73
50% glycol	6.1	10.9	17.0	1.77
75% glycol	6.7	12.2	18.9	1.82
Ethanol				
0% glycol	7.3	13.3	20.6	1.81
25% glycol	7.4	12.2	19.6	1.65
50% glycol	7.1	12.2	19.3	1.72
75% glycol	6.8	12.3	19.1	1.81
Acetone				
0% glycol	7.0	12.5	19.5	1.78
25% glycol	7.7	12.9	20.6	1.68
50% glycol	7.3	12.6	19.9	1.74
75% glycol	7.1	12.7	19.8	1.81
Untreated	6.9	12.3	19.2	1.77
Mercerized	15.9	35.4	51.3	2.22

TABLE IV-E. Effects of swelling cotton in glycerol-solvent systems on differential dyeing characteristics

Swelling system (weight %)	Dye uptake (mg/gram)			G/R value
	Red	Green	Total	
Water				
0% glycerol	6.8	12.5	19.3	1.84
25% glycerol	7.3	13.6	20.9	1.84
50% glycerol	7.0	13.9	20.9	1.96
75% glycerol	6.5	13.5	20.0	2.09
Ethanol				
0% glycerol	7.3	13.3	20.6	1.81
25% glycerol	8.1	14.1	22.2	1.74
50% glycerol	7.8	13.9	21.7	1.77
75% glycerol	6.8	13.1	19.9	1.91
Acetone				
0% glycerol	7.0	12.5	19.5	1.78
10% glycerol	6.9	13.5	20.4	1.96
Untreated	6.9	12.3	19.2	1.77
Mercerized	15.9	35.4	51.3	2.22

In general, these systems have only minor effects on the total dye uptake and the G/R value. In view of the hydrophillic nature of glycerol and glycol it was not possible to prepare solutions covering the entire composition range in all of the organic liquids chosen nor was it possible to select a wide variety of organic liquids for these studies.

UREA AND CITRIC ACID SYSTEMS

Since certain glycol and glycerol-containing systems seemed to alter the differential dyeing properties of cotton cellulose significantly, it was considered desirable to investigate other binary systems which might have similar properties. As was noted in Chapter II, systems containing citric acid and urea showed some promise as nonaqueous swelling agents as measured by the imbibition technique. A variety of binary systems containing citric acid and urea were used as pretreatments and the samples were investigated by the differential dyeing technique. The results of the dyeing experiments are shown in Tables IV-F and IV-G.

TABLE IV-F. Effects of swelling cotton in citric acid-solvent systems on differential dyeing characteristics

Swelling system (weight %)	Dye uptake (mg/gram)			G/R value
	Red	Green	Total	
Water				
0% citric acid	6.8	12.5	19.3	1.84
10% citric acid	10.7	16.0	26.7	1.45
25% citric acid	11.5	16.7	28.2	1.46
50% citric acid	11.6	17.0	28.6	1.47
Ethanol				
0% citric acid	7.3	13.3	20.6	1.81
10% citric acid	8.8	14.4	23.2	1.64
25% citric acid	7.7	13.4	21.1	1.75
50% citric acid	8.1	14.5	22.6	1.78
Acetone				
0% citric acid	7.0	12.5	19.5	1.78
10% citric acid	7.9	15.9	23.8	2.00
Untreated	6.9	12.3	19.2	1.77
Mercerized	15.9	35.4	51.3	2.22

TABLE IV-G. Effects of Swelling cotton in urea-water and urea-acetic acid systems on differential dyeing characteristics

Swelling system	Dye uptake (mg/gram)			G/R value
	Red	Green	Total	
Water				
0% urea	6.8	12.5	19.3	1.84
10% urea	6.8	13.5	20.3	1.98
25% urea	7.8	16.2	24.0	2.08
50% urea	7.3	16.5	23.8	2.23
Acetic acid				
0% urea	7.5	13.3	20.8	1.76
10% urea	7.8	14.9	22.7	1.90
Untreated	6.9	12.3	19.2	1.77
Mercerized	15.9	35.4	51.3	2.22

Aqueous systems containing urea and citric acid, which were studied for comparison purposes with the nonaqueous systems, alter the differential dyeing properties to a considerable extent. The total dye uptake is increased with both solutes; the G/R value is decreased in the case of aqueous citric acid solutions, and increased in the case of aqueous urea solutions. The decrease in the G/R value for aqueous citric acid solutions is similar to the effect of formic acid and may, by analogy, suggest a chemical reaction between cotton cellulose and citric acid. In view of the extremely mild reaction conditions, it would be advisable to investigate the interaction between cellulose and citric acid in a detailed manner. Citric acid in the organic solvents causes a minor increase in the total dye uptake, and in certain select cases an altered G/R ratio. Nonaqueous urea solutions have similar minor effects on differential dyeing properties. In

general, the effects of nonaqueous urea and citric acid solutions are of the same order of magnitude as far as total dye uptake is concerned as corresponding aqueous systems.

CYCLOHEXANONE SYSTEMS

As was indicated in Chapter II, cyclohexanone-containing organic systems are imbibed by cotton cellulose to a considerable extent. In order to determine whether such systems had an effect on the cellulose structure, certain pretreated samples were subjected to the differential dye test. In Table IV-H are shown the effects of treatment time at room temperature, while in Table IV-I are shown the effects of treatment temperature at a constant time of one hour.

TABLE IV-H. Treatment in cyclohexanone for various times at room temperature

Treatment time (hrs.)	Total dye uptake (mg/g)	G/R value
Untreated	21.0	1.74
0.2	21.2	1.82
1.0	21.2	1.83
16.0	21.4	1.86

TABLE IV-I. Treatment in cyclohexanone for one hour at several temperatures

Treatment temp (°C)	Total dye uptake (mg/g)	G/R value
Untreated	22.9	1.75
0	22.0	1.79
25	21.2	1.83
50	22.1	1.87

It is evident from the data in Tables IV-H and IV-I that the differential dyeing properties are only slightly altered by the cyclohexanone systems. The total dye uptake is not at all affected, and although the G/R ratio is increased, in the absence of an increase in the total dye uptake, it seems reasonable to assume that no decrease in crystallinity or an increase in accessibility has taken place. The increase in the G/R value would suggest some changes within the accessible areas of the cellulose as a result of the cyclohexanone-treatments. The binary systems cyclohexanone-ethanol and cyclohexanone-acetone were also studied by the differential dye method over the entire composition range. The results of these experiments are summarized in Table IV-J,

TABLE IV-J. Treatments in cyclohexanone-solvent systems

Conc. cyclohexanone (weight %)	Ethanol		Acetone	
	Total dye (mg/g)	G/R value	Total dye (mg/g)	G/R value
0	20.6	1.81	19.5	1.78
25	23.3	1.75	20.2	1.65
50	23.0	1.92	22.2	1.87
75	21.7	1.71	23.3	1.72
100	20.7	1.90	20.7	1.90

where small increases in the total dye uptake and only small and inconsistent changes in the G/R ratio can be noted.

The binary systems cyclohexanone-formic acid, cyclohexanone-acetic acid, and cyclohexanone-propionic acid were also studied over the entire composition range and the results of the differential dye test are shown in Table IV-K.

TABLE IV-K. Treatments in cyclohexanone-aliphatic acid systems

Conc. cyclohexanone (weight %)	Formic acid		Acetic acid		Propionic acid	
	Total dye (mg/g)	G/R value	Total dye (mg/g)	G/R value	Total dye (mg/g)	G/R value
0	29.9	1.22	20.8	1.76	21.6	1.69
25	32.2	0.80	20.1	1.37	22.6	1.77
50	29.1	0.90	21.7	1.64	22.1	1.75
75	30.1	0.96	21.7	1.75	21.7	1.73
100	20.7	1.90	20.7	1.90	20.7	1.90

Once again, no significant systematic changes in the differential dyeing properties resulted from pretreatments in these systems with the exception of the formic acid-containing systems. It has been mentioned previously that formic acid-containing systems represent a special case in view of their reactive nature toward cellulose.

Thus, although it has been shown in Chapter II that cyclohexanone and binary nonaqueous systems containing cyclohexanone are significantly imbibed by cotton cellulose, the differential dye test indicates that such imbibition or reagent penetration does not cause a fundamental change in the cellulose physico-chemical structure. A similar conclusion was drawn on the basis of reactivity studies as discussed in Chapter VI.

CHAPTER V. DERIVATIVE FORMATION

GENERAL CONSIDERATIONS

The concept of partially disrupting the cellulose structure by means of derivative formation followed by removal of the substituent groups seemed worthy of investigation. It is well agreed that the major or for that matter the only retardant to complete cellulose reactivity is the extensive hydrogen bonding network through both the amorphous and crystalline regions. Were it not for this interchain bonding, swelling and reactive reagents could easily penetrate the cellulose structure. The formation by suitable chemical reactions of a partial derivative should achieve a disruption of the interchain bonding network. Upon removal, again by suitable chemical reactions of the substituents, the cellulosic network might remain disrupted and thus be in a somewhat more accessible form. Aiken (1) studied the effect of acetylation on water binding and physical properties of cellulose, and indicated enhanced properties at low degrees of substitution. In a recent publication Nevell and Zeronian (9), suggested that a small increase in hygroscopicity occurs during the very early stages of acetylation of cotton.

In this work it was decided to utilize the autocatalytic formylation of cellulose following essentially the procedure developed by Nickerson (10). The working hypothesis was to achieve low levels of formylation which was followed by the removal of the formyl groups via an alkaline catalyzed saponification. The properties of both the formylated and formylated-saponified samples were investigated in order to determine whether such a series of reactions achieved the desired result of cellulose network disruption. The several samples were studied by differential dyeing as described in Chapter IV, imbibition tests as described in Chapter II, and characterized by an evaluation of fiber mechanical properties.

EXPERIMENTAL AND RESULTS

Five gram samples of cotton were treated with 200 ml. of 88% commercial grade formic acid at several temperatures and for various times. The reaction product was filtered on a glass filter, washed with water to remove excess acid, and allowed to air dry overnight. The degree of formylation achieved was analytically determined by means of a modified Eberstadt alkaline catalyzed standard saponification method. The degree of formylation is shown in Table V-A.

TABLE V-A. Combined formic acid (%)

Time	0 °C	25° C	50° C
0.2 hours	1.05	1.93	1.98
1.0 hours	1.60	2.36	3.10
16.0 hours	2.22	3.72	4.77

As can be seen from these data, only extremely low D.S. values were achieved, the highest combined formic acid content of 4.77% corresponding to a value of 0.17 D.S. units.

Subsamples of the formylated samples were saponified by a procedure virtually identical with that used for the estimation of the degree of formylation. The saponification of the formylated samples involved the treatment of 1.5 grams of formylated sample in a solution containing 30 ml. water, 30 ml. ethanol, and 75 ml. 0.1 N NaOH for two hours under reflux at 50° C. After filtration, the saponified samples were washed with water, soured with 1% acetic acid, washed again with water, and air dried overnight.

The formylated and the formylated-saponified samples were subjected to the differential dye test and the water of imbibition test, and the data are shown in Tables V-B and V-C.

TABLE V-B. Properties of formylated cotton

Formic acid treatment (time/temp)	Combined HCOOH(%) before sapon.	Water of imbibition (%)	Differential dye test			
			Dye uptake		(mg/g) total	G/R value
			red	green		
none	0	33.5	8.4	14.5	22.9	1.72
0.2/0	1.05	47.7	12.5	17.8	30.3	1.41
1.0/0	1.60	47.8	14.1	19.9	34.0	1.40
16.0/0	2.22	56.7	17.2	22.8	40.0	1.32
0.2/25	1.93	46.7	14.4	19.3	33.7	1.34
1.0/25	2.36	50.0	15.1	20.4	35.5	1.35
16.0/25	3.72	55.3	21.0	22.9	43.8	1.09
0.2/50	1.98	49.8	14.1	20.7	34.8	1.46
1.0/50	3.10	52.1	18.9	20.7	39.6	1.10
16.0/50	4.77	59.1	20.5	22.9	43.4	1.11

TABLE V-C. Properties of formylated-saponified cotton

Formic acid treatment (time/temp)	Combined HCOOH(%) before sapon.	Water of imbibition (%)	Differential dye test			
			Dye uptake		(mg/g) total	G/R value
			red	green		
none	0	41.6	9.0	19.7	28.7	2.18
0.2/0	1.05	57.6	8.1	17.5	25.6	2.14
1.0/0	1.60	58.1	8.5	18.9	27.4	2.22
16.0/0	2.22	60.3	7.7	19.3	27.0	2.48
0.2/25	1.93	59.1	8.9	17.9	26.8	2.00
1.0/25	2.36	58.3	9.1	20.1	29.2	2.20
16.0/25	3.72	57.2	7.6	18.2	25.8	2.36
0.2/50	1.98	51.4	7.9	16.5	24.4	2.07
1.0/50	3.10	50.2	8.8	19.0	27.8	2.15
16.0/50	4.77	51.2	7.6	17.6	25.2	2.29

Examination of the data in Table V-B reveals that formylation of cotton to low degree of substitution levels increases the water of imbibition and both the green and red dye uptake during the differential dye test. The distribution of the two dyes, as indicated by the G/R value, is also affected by the formylation resulting in a decrease in the G/R value. The relationship between the degree of formylation and the total dye uptake is shown graphically in Figure 14. While the total dye uptake increases with increasing formylation, it is not possible to ascribe this behavior solely to an increase in accessibility. If the formylation resulted in an increase in accessibility, it would be expected that the G/R value would also increase, or at least remain constant. As shown in

Figure 15, the G/R value actually decreases with increasing formylation. The changes in the differential dyeing properties of the formylated samples must be ascribed, in part at least, to the introduction of new dye sites which are preferential for the red dye.

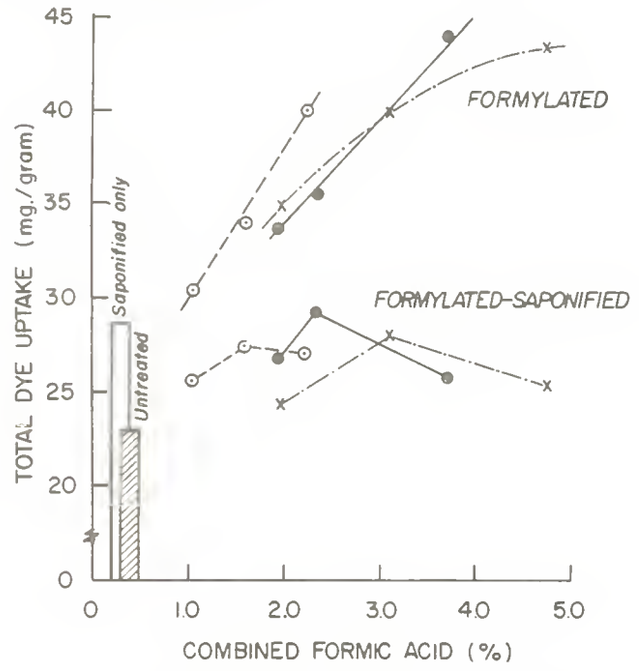

Figure 14. Total dye uptake as a function of combined formic acid. Formylation temperature: 0 = 0° C.; ● = 25° C.; x = 50° C.

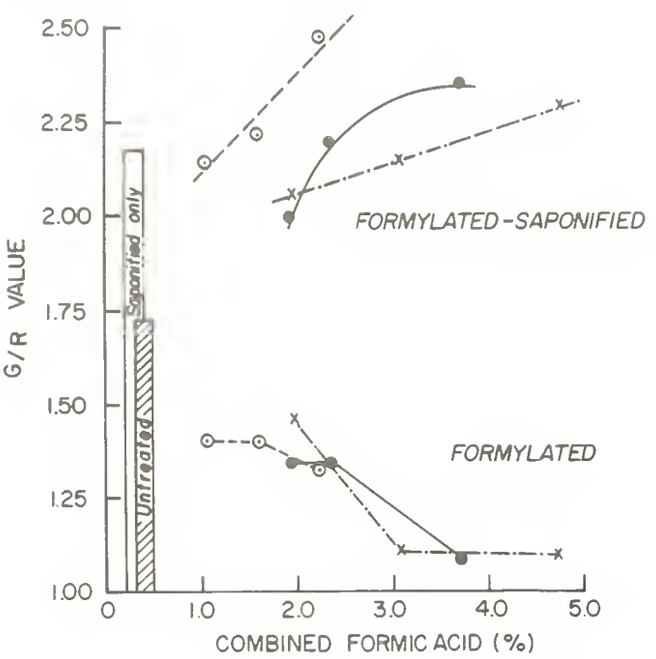

Figure 15. G/R ratio as a function of combined formic acid. Formylation temperature: 0 = 0° C.; ● = 25° C.; x = 50° C.

Further evidence for this mechanism may be found in considering the differential dyeing properties of the samples where the formyl groups were subsequently removed by saponification (Table V-C). Here we find that the total dye uptake has been reduced once again and the G/R value has increased. An interesting effect of the degree of formylation on the total dye uptake is that at each formylation temperature the total dye uptake goes through a maximum, indicating that differential dyeing is influenced by both degree of formylation and the temperature at which the esterification is performed. Although the dye uptake for the formylated-saponified samples is not appreciably different from a sample which had received the saponification treatment but no prior formylation, the G/R value of these samples is clearly dependent upon the extent of prior formylation.

That some increase in accessibility is brought about by the reaction with formic acid is evident from the water of imbibition values as shown in Tables V-B and V-C and illustrated graphically in Figure 16. The

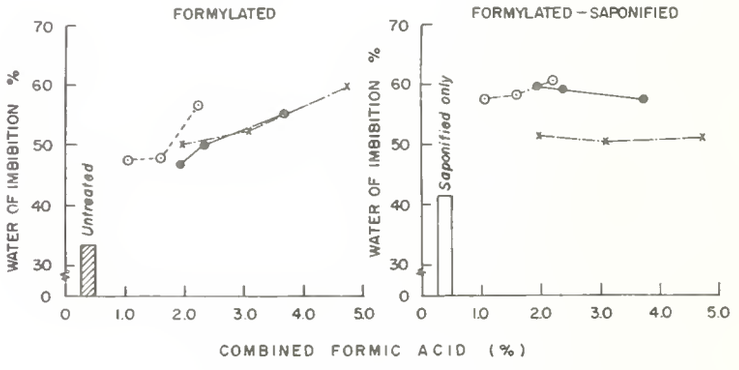

Figure 16. Water of imbibition as a function of combined formic acid. Formylation temperature: 0 = 0° C.; ● = 25° C; x = 50° C.

water of imbibition increases with increasing formylation, indicating that the esterified cotton samples have more open structures which are penetrable by reagents such as water. Removal of the formyl groups by saponification maintains this more accessible structure as again indicated by the water of imbibition values. The saponification

process itself increases the water of imbibition, but much greater increases are realized for samples which had received the formylation although a dependence upon the extent of formylation is not evident.

It is of interest to note the effect of temperature during formylation on the increase in the ability of the material to imbibe water upon subsequent saponification of the ester group. Apparently lower temperatures of formylation result in greater increases in the water of imbibition and, as may be seen in Table V-C and in Figure 16, the formylation at 50° C. resulted in the lowest water of imbibition values.

The single fiber mechanical properties of the formylated and formylated-saponified samples were evaluated on an Instron tensile tester by the procedure described in greater detail in Chapter VII. Samples which were formylated at 50° C. were chosen for these tests and the data are shown in Table V-D.

TABLE V-D. Single fiber mechanical properties

	Combined HCOOH (%)	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (Mg/cm^2)
Formylated				
blank	0	40.1	5.42	111.0
0.2/50	1.98	38.0	5.10	130.1
1.0/50	3.10	41.7	5.38	116.6
16.0/50	4.77	27.7	4.32	99.8
Formylated-Saponified				
blank	0	40.1	6.25	91.8
0.2/50	1.98	44.6	4.79	169.6
1.0/50	3.10	34.8	4.86	121.9
16.0/50	4.77	28.5	4.78	108.7
Pooled 95% conf. limit		4.2	0.48	16.1

Fiber strength was not adversely affected by this treatment except at the highest level of formylation. The fiber extension at break was not significantly decreased, although the anticipated increase in extensibility was not realized. Fiber stiffness, as estimated by the elastic modulus, remained essentially unaltered. In general, it appears that this type of reaction sequence may be performed without impairing fiber mechanical properties, although beneficial effects will probably not be achieved by this route.

CONCLUSION

It may be concluded on the basis of these preliminary studies that the process of low level substitution followed by removal of the substituent groups results in a material of higher accessibility and therefore represents a potential general method for increasing cotton cellulose reactivity. The formylation reaction described here may not represent the ideal reaction sequence; however, it appears reasonable to conclude that an esterification rather than an etherification be employed in view of the relative ease of removal of ester groups. It is recommended that the approach of partial derivative formation followed by the removal of the substituent group be given further intensive consideration as a means for increasing the penetrability and reactivity of cotton cellulose.

CHAPTER VI. REACTIVITY STUDIES

GENERAL CONSIDERATIONS

Cellulose undergoes chemical reactions characteristic of a polyhydric alcohol. The rates of such reactions and the degree of completion which the reaction attains are governed to a large extent by the accessibility of the cellulosic hydroxyl groups to the chemical reagents. It has been well established that only a fraction of the hydroxyl groups in a native cotton cellulose is available for reaction in view of an extensive hydrogen bonding network which, in the extreme, results in crystalline domains which are essentially impenetrable to chemical reagents. In order to achieve useful chemical modifications of cotton cellulose, the normal accessibility of the material needs to be increased by a swelling pretreatment. By the same token the extent of chemical reaction which takes place under standardized conditions may be used as a means of characterizing the effectiveness of a particular swelling pretreatment to which the cotton cellulose may have been subjected. Such an approach to studying pretreatments was adopted and is discussed in this chapter. Two distinctively different chemical reaction systems were chosen for study. One of these, a methylation reaction, represents an alkaline catalyzed etherification reaction. At first the methylation reaction was intended only as a means of studying effectiveness of pretreatments, but it was seen that the methylation system itself was clearly a nonaqueous swelling system. This reaction was therefore studied in detail. The other reaction was a standardized formylation, which was used to characterize swelling pretreatments and which represents an acid catalyzed esterification.

METHYLATION

In a normal cellulose methylation reaction, the cellulose is impregnated with 40% (by weight) aqueous NaOH and then allowed to react in toluene containing dimethyl sulfate. The methyl cellulose which is obtained is a partial derivative with a degree of substitution (D.S.) ranging from 0.5 to 1.5. Complete methylation, i.e., D.S. = 3.0, can be achieved only by repeated methylations. The product obtained by a one-step methylation with dimethyl sulfate in toluene is characteristic of a heterogeneously substituted partial cellulose derivative. In view of the topochemical nature of the reaction, the surface of certain morphological domains (fiber, fibril, micelle, or crystallite) is preferentially methylated, leaving an inner unreacted core. In such a reaction only a small fraction of the total cellulosic hydroxyl groups is available for reaction. If the methylation system is one which is capable of disrupting lateral order, i.e., if it is a swelling system, then the product of the reaction should be more characteristic of a homogeneously substituted partial cellulose derivative. As swelling increases, the surface-core nature of the cellulosic substrate ceases to predominate and a larger fraction of the cellulosic hydroxyl groups becomes available for reaction. In such a swollen system the partial substitution of the hydroxyl groups is more nearly governed by reaction rate ratios of the three hydroxyl groups in each anhydroglucose unit, and by the laws of probability, than by hydroxyl group availability. In the extreme, the partial substitution of a homogeneously dispersed cellulose will be governed only by reaction rates and probability theory. One may thus be able to study the extent of swelling during reaction by examining the distribution of substituents in the partial derivative and comparing the experimental distribution with a theoretical distribution.

The theoretical distribution is calculated from the laws of probability assuming that all the hydroxyl groups are free and available for reaction and that the ratio of reaction rate constants for the three hydroxyl groups in each anhydroglucose unit is 1:1:1. The distribution of substituents in partial cellulose derivatives and the method of computing theoretical distributions have been previously discussed in detail (16).

In the methylation experiments a 1-gram sample of the cotton cellulose is treated with 60 ml. of a 40% (by weight) NaOH solution (aqueous) for 30 minutes, squeezed to remove excess NaOH, allowing the sample with the NaOH to weigh approximately 10 grams, and reacted at room temperature for 5 hours in 100 ml. of toluene containing dimethyl sulfate. After the prescribed reaction time, the sample is washed in boiling distilled water until the wash water is neutral, air dried, and ground in a Wiley mill to achieve sample uniformity. The degree of methoxyl substitution is determined by the classical Zeissel alkoxyl content, analytical procedure (4).

In a series of preliminary experiments cotton samples which had received several types of aqueous pretreatments were subjected to the methylation procedure at two levels of dimethyl sulfate concentration. The results of these experiments are presented in Table VI-A.

TABLE VI-A. Preliminary methylation studies, degree of methoxyl substitution

Preswelling condition	Dimethyl SO_4 concentration	
	9% (vol.)	27% (vol.)
Untreated	0.70	1.02
Mercerized	0.46	0.78
10 M urea-treated	0.55	1.05
10 M urea & mercerized	0.34	1.88

For each sample the higher dimethyl sulfate concentration resulted in a higher degree of substitution. While this was to be expected, it is interesting to note that the degree of substitution values for the preswollen cellulose samples are significantly lower than the value for the untreated material. One might at first expect that in view of the preswelling more hydroxyl groups would be available for methylation, allowing a higher degree of substitution to be attained. The opposite result was observed. If one considers that because of the larger number of available hydroxyl groups in a preswollen cellulose there is a lower reagent concentration per active site (i.e., per hydroxyl group), then the lower degree of substitution is not unreasonable. It should be borne in mind, however, that in all methylation experiments the NaOH and dimethyl sulfate are in large excess relative to the cellulose. These results indicate that the degree of methylation is significantly affected by the preswelling history of the cellulosic material.

The manner in which the methoxyl groups distribute themselves along the cellulose chains at any D.S. value should be a more sensitive estimate of preswelling than the actual D.S. value itself. The distribution of methoxyl groups in a partially methylated cellulose can be determined by suitable chromatographic separation of trimethyl, dimethyl, monomethyl, and unsubstituted glucose residues which are obtained upon acid hydrolysis of the partial cellulose derivative. The distribution which is obtained experimentally may then be compared with the theoretical distribution calculated on the basis of random substitution, equal and total availability of all cellulosic hydroxyl groups, and equality and constancy of the rate constants for methylation of the three types of cellulosic hydroxyl group.

In Table VI-B are shown the results of duplicate analyses of the distribution of substituents for two samples - cotton with no preswelling treatment and a cotton sample which had been preswollen with the combination 10 M urea and mercerization treatment. The theoretical distributions, based on the assumptions mentioned above, are also shown for each sample. Although the experimental D.S. values for the two samples are quite different, comparison should be made between the experimental values and the theoretical values for each sample. The heterogeneous methylation of the untreated cotton results in a sample which is topochemically substituted as evidenced by the large trimethyl glucose fraction. The preswelling treatment (10M urea and mercerization) did not significantly alter the topochemical nature of the methylation.

TABLE VI-B. Preliminary methylation studies, distribution of substituents

	Untreated cotton D.S. = 0.87		10 M Urea & mercer. cotton D.S. = 0.67	
	Exper.	Theor.	Exper.	Theor.
Glucose	48.4	35.8	65.9	47.0
Mono CH_3 gluc.	10.4	43.9	9.9	40.4
Di CH_3 gluc.	17.2	17.9	9.2	11.5
Tri CH_3 gluc.	24.0	2.4	15.0	1.1

As shown in Table VI-A, a higher level of methylation was achieved with a 27% dimethyl sulfate than with a 9% dimethyl sulfate solution in toluene. It was of interest to determine more exactly the effects of varying the concentration of dimethyl sulfate in toluene on the nature of the reaction. Toward this end methylations were conducted in the following systems:

10% dimethyl sulfate (volume) in toluene
50% dimethyl sulfate (volume) in toluene
100% dimethyl sulfate

An untreated cotton sample and samples which had been subjected to two types of mercerization were used in these methylation experiments. Both mercerizations involved the treatment in 20% (by weight) NaOH under slack conditions, at room temperature for five minutes, washing, souring in 1% acetic acid and finally washing with distilled water. In one mercerization the sample is allowed to air dry directly from the final water wash. In the other mercerization treatment the final wash water is replaced by acetone which in turn is replaced by diethyl ether, and the sample is finally allowed to dry from diethyl ether. The mercerization sample dried from water is designated mercerized air, while the mercerized sample where the water is removed by the technique of solvent replacement and finally dried from ether is designated mercerized solvent. The degree of methoxyl substitution was determined in duplicate and the results are tabulated in Table VI-C.

TABLE VI-C. Degree of methoxyl substitution

	Dimethyl sulfate-toluene		
	10%	50%	100%
Untreated (1)	0.67	1.02	1.31
(2)	0.59	0.99	1.31
Avg.	0.63	1.00	1.31
Mercerized air (1)	0.57	0.78	1.24
(2)	0.57	0.75	1.16
Avg.	0.57	0.76	1.20
Mercerized solvent (1)	0.57	0.76	1.42
(2)	0.59	0.78	1.38
Avg.	0.58	0.77	1.40

Higher degrees of substitution are again achieved with higher concentrations of dimethyl sulfate as was indicated by the results of the preliminary studies in Table VI-A. The further preliminary observation that preswelling treatments decrease the achieved D.S. value at any given dimethyl sulfate concentration is also essentially verified by these experiments especially at low dimethyl sulfate concentration.

The methylated samples were subjected to complete acid hydrolysis and the resultant sugars were quantitatively analyzed by the application of paper partition chromatographic techniques. The chromatographic analysis data are presented in Tables VI-D, VI-E, and VI-F, along with the theoretical

TABLE VI-D. Distribution of substituents; 10% dimethyl sulfate in toluene.
Sugar components in mole percent

	D.S.	Glucose	Mono CH_3 gluc.	Di CH_3 gluc.	Tri CH_3 gluc.
Untreated					
experimental	0.63	69.7	8.2	8.0	14.1
theoretical	0.66	49.9	39.0	10.2	0.9
Mercerized air					
experimental	0.57	72.3	9.3	6.2	12.2
theoretical	0.59	53.1	37.4	8.8	0.7
Mercer. solvent					
experimental	0.58	71.8	10.1	5.0	13.0
theoretical	0.59	53.1	37.4	8.8	0.7

TABLE VI-E. Distribution of substituents; 50% dimethyl sulfate in toluene.
Sugar components in mole percent

	D.S.	Glucose	Mono CH_3 gluc.	Di CH_3 gluc.	Tri CH_3 gluc.
Untreated					
experimental	1.00	40.4	26.6	21.1	11.9
theoretical	1.04	30.1	44.4	21.9	3.6
Mercerized air					
experimental	0.76	55.8	21.6	12.6	10.0
theoretical	0.77	42.2	42.2	14.1	1.6
Mercer. solvent					
experimental	0.77	58.2	20.8	10.3	10.6
theoretical	0.73	40.5	42.7	15.0	1.8

TABLE VI-F. Distribution of substituents; 100% dimethyl sulfate in toluene.
Sugar components in mole percent

	D.S.	Glucose	Mono CH_3 gluc.	Di CH_3 gluc.	Tri CH_3 gluc.
Untreated					
experimental	1.31	33.8	19.2	26.2	20.7
theoretical	1.33	17.8	41.6	32.2	8.4
Mercerized air					
experimental	1.20	35.8	19.3	26.6	18.4
theoretical	1.27	21.6	43.2	28.8	6.4
Mercer. solvent					
experimental	1.40	33.1	17.6	23.5	25.8
theoretical	1.41	14.9	39.6	35.1	10.4

methoxyl distribution values for the particular degree of substitution which had been achieved in the methylation. The theoretical methoxyl degree of substitution is a value calculated from the chromatographic distribution analyses. The correspondence between the theoretical degree of substitution and the degree of substitution determined by the Zeissel methoxyl analyses method attests to the accuracy of the chromatographic procedure. The chromatographic analysis was carried out in duplicate for each sample and excellent reproducibility was attained.

In examining the data in Tables VI-D, VI-E, and VI-F, attention should be given to a comparison between the theoretical and experimental distributions for each sample at each dimethyl sulfate concentration. Such a comparison is presented in Table VI-G where the ratio of experimental to theoretical is given for each of the conditions. Particular attention should be given to the trimethylglucose values which indicate that the greatest deviation between the experimental and theoretical distributions are found for samples methylated with 10% dimethyl sulfate in toluene. Smaller deviations are obtained when methylation was conducted in either the 50% or 100% dimethyl sulfate. These observations indicate that during methylation with either 50% or 100% dimethyl sulfate a more random distribution of substituents was attained than in the methylation with 10% dimethyl sulfate. In order for this greater randomness to be possible, a larger fraction of the cellulosic hydroxyl groups had to be available for reaction, i. e., a greater degree of swelling occurred with the higher dimethyl sulfate concentration.

TABLE VI-G. Ratios of experimental to theoretical distribution values for various methylation conditions

DMS conc. %	Glucose			MonoCH_3gluc.			DiCH_3gluc.			TriCH_3gluc.		
	U	MA	MS	U	MA	MS	U	MA	MS	U	MA	MS
10	1.4	1.4	1.4	.21	.24	.27	.8	.7	.6	16	17	18
50	1.3	1.3	1.4	.60	.51	.48	.6	.9	.7	3.3	6.2	6.0
100	1.9	1.7	2.2	.46	.44	.44	.8	.9	.7	2.4	2.8	2.4

U = untreated; MA = mercerized, air dried; MS = mercerized, solvent dried

On the basis of these methylation experiments, the dimethyl sulfate-toluene system suggests itself as a potential cellulose reactive swelling system. Other experiments with this system are discussed in Chapters II and III, and yield essentially the same conclusion.

FORMYLATION

As another means for studying the effectiveness of various pretreatments, a standard formylation technique was adopted. The reaction between formic acid and cellulose was studied by Nickerson (10) as a means of determining cellulose accessibility. Based upon the results presented in Chapter V, the following procedure was adopted as a standard formylation. A one-gram sample of cotton was immersed in 50 ml. of 88% commercial grade formic acid for one hour at 50° C. The sample was then filtered, washed free of acid and allowed to dry. The degree of formylation was estimated by a modified Eberstadt saponification technique using NaOH in aqueous ethanol and is expressed in the following tables as combined formic acid in percent.

Samples of cotton were subjected to a large number of pretreatment systems in order to determine whether these pretreatments caused a sufficient degree of swelling to be manifest as an increase in reactivity toward the formylation. It will be noted that

the pretreatments were chosen on the basis of other experiments which had indicated these systems to be potentially useful nonaqueous swelling reagents. The results of the standard formylation experiments of an untreated sample and two mercerized samples are presented in Table VI-H. It will be seen that both types of mercerization increased the reactivity of the cotton cellulose toward the standard formylation.

TABLE VI-H. Standard formylation

Pretreatment	Combined formic acid (%)
Untreated	4. 25
Mercerized, air	8. 13
Mercerized solvent	7. 60

In the case of the nonaqueous pretreatments the following systems and procedure were adopted. Tartaric acid, citric acid, and glycerol dissolved in acetone, ethanol, cyclohexanol and cyclohexanone constituted the binary systems investigated. One-gram samples to be pretreated were exposed to the system (35 ml.) for one hour at room temperature and subsequently washed with either acetone or ethanol. Acetone was used for washing when either acetone or cyclohexanone was a component in the binary system, while ethanol was used for washing when either ethanol or cyclohexanol was a component in the binary system. The washing step was performed with three separate fresh portions of the wash liquid. The results of the standard formylation are presented in Table VI-I. No change in reactivity was caused by any of the nonaqueous pretreatments despite the fact that these systems were chosen on the basis of their ability to penetrate cotton cellulose as indicated by the imbibition measurements discussed in Chapter II. It must be concluded that while these binary systems penetrate the cellulose substrate, they do not cause a permanent or for that matter even a temporary increase in reactivity. This observation would suggest that these binary systems penetrate only the easily accessible amorphous regions of the cotton cellulose.

TABLE VI-I. Standard Formylation

Solute	Solvent			
	Acetone	Ethanol	Cyclohexanone	Cyclohexanol
None	-	-	4. 30	4. 28
2% Tartaric acid	4. 40	4. 33	4. 28	4. 09
10% Citric acid	4. 29	4. 25	4. 30	4. 15
2% Glycerol	4. 28	4. 28	4. 14	4. 25

CHAPTER VII. MECHANICAL PROPERTIES

GENERAL CONSIDERATIONS

It is well known that the physico-chemical structure of textile fibers is reflected in mechanical properties. It is therefore to be expected that any changes which are brought about in a fiber's physico-chemical structure will be evident as changes in mechanical properties. To the extent that some of the chemical swelling treatments, discussed in the previous chapters, cause significant alterations in the fiber's physico-chemical structure, such structural alterations may be evident as changes in mechanical properties. It is also of interest and of practical importance to determine the effects of chemical treatments on mechanical properties with a view toward the enhancement of certain desirable characteristics by such chemical treatments. The fact that swelling treatments significantly affect mechanical properties of cotton fibers and yarns is well established for aqueous systems.

The effects of mercerization on the mechanical properties of cotton fibers and yarns has been discussed by many workers (15), and relationships have been established between the extent of structural modification during mercerization and the changes in the mechanical properties. The changes in mechanical properties due to mercerization are largely a result of a significant decrease in cellulose crystallinity, and changes in the fibrillar orientation which are dependent upon the tension during the treatment. Nonaqueous decrystallizing chemical treatments have been discussed and the changes in mechanical properties which are observed are quite similar to those obtained upon aqueous mercerization (19, 20). The chemical treatments used in the study reported here are much milder than the nonaqueous decrystallizing systems and thus similar changes in mechanical properties are not to be expected. Most of the systems were evaluated by the measurement of yarn rather than single fiber mechanical properties in order that a larger number of systems could be studied.

YARN MECHANICAL PROPERTIES

A 40/3 Supima cotton yarn[1] was used for these experiments and was extracted in chloroform prior to the treatment in the nonaqueous system. The treatment consisted of immersing approximately 10-inch specimens in the reagent under completely relaxed conditions for one hour at room temperature. The thoroughly soaked yarn specimens were subjected to load-extension tests on an Instron tensile tester at a 10% per minute rate of extension, the test length being 5 inches. The linear density of the yarn, determined at standard conditions (70° F., 65% R. H), was used to normalize the load-extension properties in order to obtain the following parameters: tenacity at break, extension at break, and elastic modulus. The results shown in the tables of data are the means of ten single-strand tests.

The single component nonaqueous systems had minor effects on the yarn mechanical properties as indicated by the data in Table VII-A. Treatment in water slightly increased the strength, increased the extensibility by a factor of two, and decreased the elastic modulus by the same order of magnitude. While some of the organic reagents increased both strength and extensibility, such increases, especially in extensibility, were much lower than those resulting from the water treatment. Cyclohexanol and formic acid decreased strength, although such strength losses are barely significant statistically. A major increase in yarn extensibility resulted from the formic acid, while the other two aliphatic acids increased extensibility to a lesser extent. With the exception of cyclohexanol, treatment in the

1/ Supplied through the courtesy of The American Thread Co.

TABLE VII-A. Mechanical properties of yarns treated in single component nonaqueous systems

Treatment	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (g/tex)
Untreated	29.0±0.9	6.0±0.2	562±16
Water	31.6 1.4	12.4 0.4	282 3
Acetone	29.7 1.3	7.9 0.3	477 19
Ethanol	30.3 1.2	9.0 0.4	399 30
Cyclohexanone	31.2 1.1	7.9 0.3	498 15
Cyclohexanol	27.0 1.3	7.2 0.4	545 32
Formic acid	27.2 2.4	11.4 0.6	312 32
Acetic acid	31.2 1.4	9.4 0.6	370 32
Propionic acid	30.7 1.6	8.1 0.4	448 19

nonaqueous reagents resulted in a lower elastic modulus, such decreases frequently approximating that due to the water treatment.

In Table VII-B are shown the mechanical properties of yarns treated in 1:1 mixtures by weight of several organic solvents in

TABLE VII-B. Mechanical properties of yarns treated in 1:1 mixtures of organic solvents

Treatment	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (g/tex)
Untreated	29.0±0.9	6.9±0.2	562±16
Water	31.6 1.4	12.4 0.4	282 3
Cyclohexanol: acetone	31.4±1.3	8.1±0.2	502±15
Cyclohexanol: ethanol	30.0 0.7	7.2 0.2	538 17
Cyclohexanol: formic acid	28.0 0.8	8.1 0.4	417 21
Cyclohexanol: acetic acid	29.6 1.3	6.5 0.1	586 9
Cyclohexanol: propionic acid	28.6 1.0	6.4 0.3	587 16
Cyclohexanone: acetone	30.0±1.2	7.0±0.1	560±11
Cyclohexanone: ethanol	30.6 1.6	7.1 0.4	511 19
Cyclohexanone: formic acid	28.0 0.8	8.8 0.2	379 8
Cyclohexanone: acetic acid	31.3 1.1	7.3 0.3	505 24
Cyclohexanone: propionic acid	31.4 1.5	7.2 0.2	534 14

cyclohexanone and cyclohexanol. It is readily apparent that the effects of the 1:1 mixtures on yarn mechanical properties are also minor. Systems containing formic acid result in a strength decrease, although in such cases there is an increase in extensibility and a decrease in elastic modulus. In general, when cyclohexanol was used as a solvent the strength values are somewhat lower than when cyclohexanone was the solvent. The effects of other binary systems are indicated in Table VII-C where citric acid, tartaric acid, urea, and glycerol are considered as solutes in acetone, ethanol, cyclohexanone, and cyclohexanol.

TABLE VII-C. Mechanical properties of yarns treated in various binary nonaqueous systems

Treatment	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (g/tex)
Untreated	29.0±0.9	6.9±0.2	562±16
Water	31.6 1.4	12.4 0.4	282 3
10% Citric acid in acetone	29.8±0.9	6.9±0.2	538±19
10% Citric acid in ethanol	28.1 1.7	7.3 0.5	458 24
10% Citric acid in cyclohexanone	30.8 0.8	6.9 0.2	551 11
10% Citric acid in cyclohexanol	27.4 1.5	6.4 0.2	599 16
2% tartaric acid in acetone	24.7±1.1	6.6±0.2	488±18
2% tartaric acid in ethanol	25.3 1.4	7.4 0.6	434 38
2% tartaric acid in cyclohexanone	30.9 1.0	7.0 0.2	568 20
2% tartaric acid in cyclohexanol	30.3 1.1	6.7 0.3	590 18
20% tartaric acid in ethanol	29.8±1.0	7.7±0.3	488±10
2% glycerol in acetone	32.5±1.2	9.4±0.5	417±28
2% glycerol in ethanol	33.0 1.6	9.5 0.5	341 12
2% glycerol in cyclohexanone	30.0 0.9	7.3 0.2	494 19
2% glycerol in cyclohexanol	28.4 1.3	6.8 0.3	594 26
20% glycerol in ethanol	31.0±1.3	8.7±0.5	392±27
0.5% urea in acetone	32.1±1.3	8.3±0.6	460±44
5.0% urea in ethanol	32.6 1.3	10.6 0.4	320 10
0.1% urea in cyclohexanone	30.6 0.9	7.1 0.2	541 14
1.0% urea in cyclohexanone	28.4 0.9	6.5 0.2	600 11

It is of interest to note that treatments in 2% tartaric acid solutions in both ethanol and acetone had the greatest degradative effects, while tartaric acid in either cyclohexanone or cyclohexanol resulted in no change in strength or extensibility. On the other hand, treatments in 2% glycerol in both acetone and ethanol increased yarn strength and extensibility, while glycerol in cyclohexanone or cyclohexanol again had no effect. Surprisingly, citric acid solutions in all of the organic solvents had no effect on mechanical properties and it should also be noted that urea in acetone or ethanol increased both strength and extensibility. In nearly all cases extensibility and elastic modulus followed their well known inverse interrelationship - increases in extensibility being accompanied by decreases in elastic modulus. These results indicate that certain select

nonaqueous binary systems have a good potential for enhancing mechanical properties of cotton. These data further indicate that none of the systems which have been investigated have sufficiently pronounced degradative effects to eliminate them from consideration as nonaqueous swelling agents on the basis of mechanical properties.

In Chapter VI the methylation of cotton cellulose in dimethyl sulfate-toluene systems was discussed, while the effects on dimensional properties of fibers of such systems were treated in Chapter III. The data clearly suggested a significant swelling effect which was strongly dependent upon the concentration of the dimethyl sulfate in toluene. It was of interest, therefore, to determine the effects of the dimethyl sulfate-toluene system on the mechanical properties of yarns. The experimental treatment conditions were identical with those described above, and the method of yarn property evaluation was also as discussed above. The data are presented in Table VII-D and are graphically illustrated in Figure 17.

TABLE VII-D. Mechanical properties of yarns treated in dimethyl sulfate-toluene systems

Treatment Conc. $DiCH_3SO_4$ (wt. %)	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (g/tex)
Untreated	30.1±1.1	7.4±0.3	546±17
Water	31.8±1.4	11.9±0.5	289± 4
0	30.2±0.8	7.3±0.2	549±14
1	23.6 1.3	6.1 0.4	558 20
2	18.4 0.9	5.5 0.4	518 10
5	16.4 0.8	5.5 0.3	469 13
10	12.7 0.4	5.0 0.2	406 17
20	9.3 0.6	4.4 0.2	342 15

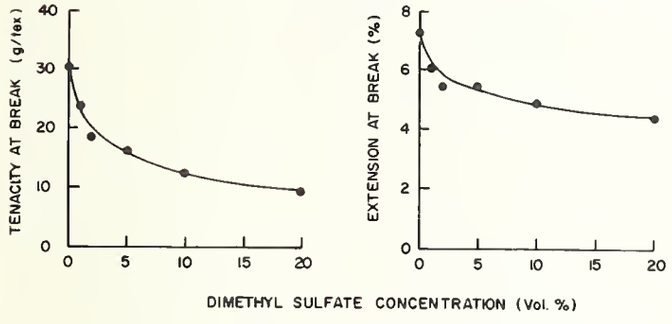

Figure 17. Yarn mechanical properties as a function of dimethyl sulfate concentration in toluene

It is evident from the data that the dimethyl sulfate-toluene system strongly degrades cotton cellulose as indicated by decreases in yarn tenacity, extension at break, and elastic modulus. The extent of degradation caused by the one-hour treatment is highly dependent upon the dimethyl sulfate concentration. Although no alkaline catalyst was used, it is possible that the treatment results in a methylation of the cotton cellulose forming a partial methyl cellulose derivative (Chapter VI), and that this derivative formation results in a disruption of the hydrogen bonding network within the cellulose matrix. Some of the losses in yarn mechanical properties may therefore be ascribed to this effect of H-bond disruption due to derivative formation. It is, however, strongly suspected that the major portion of the strength loss is a result of some other mechanism resulting in cellulose degradation, with this mechanism presumably being hydrolytic in character.

FIBER MECHANICAL PROPERTIES

The effects on the mechanical properties of single cotton fibers of several nonaqueous single component and binary systems were also investigated. Bulk cotton samples were soaked in the system under study for one hour and subsequently washed in the corresponding solvent, dried, and conditioned in a standard atmosphere. Fifty single fibers from each of the treated samples were randomly selected and their mechanical properties evaluated by the standard TRI technique which has been previously described in detail (24). The data are summarized in Table VII-E and clearly indicate that none of the treatments adversely affect single fiber mechanical properties. It is also of importance to observe that the treatments do not exert a beneficial effect such as a significant increase in extensibility or a major decrease in the elastic modulus. These observations indicate that the treatments do not alter the cellulosic structure drastically. Single fiber mechanical properties were also evaluated for some of the formylated and formylated-saponified cotton samples, and these results have been discussed in Chapter V.

TABLE VII-E. Fiber mechanical properties

Treatment	Tenacity at break (g/tex)	Extension at break (%)	Elastic modulus (Mg/cm^2)
Untreated	40.1	5.42	111.0
Acetone - 25° C	33.7	5.45	87.1
Acetone - reflux	37.7	4.80	116.3
Acetic acid - 25° C.	37.2	4.75	115.9
10% Citric acid in acetone-25° C	37.3	5.47	98.4
20% Citric acid in acetone-reflux	35.9	5.21	106.8
7% Citric acid in acetic acid-25° C	34.2	5.01	101.4
Pooled 95% conf. limit	4.2	0.47	13.8

CHAPTER VIII.
CONCLUSIONS AND RECOMMENDATIONS

The experiments which were conducted in conjunction with this research program were designed to shed some light on the question relative to the ability of nonaqueous liquid systems to swell cotton cellulose. As previously stated, the assumption was made that swelling was of interest only insofar that it indicated the potentialities of a given system to increase cotton cellulose reactivity. Several of the methods which were used in the course of this work to study the effects of various nonaqueous treatments were designed to characterize reactivity increases rather than volume changes.

Although attempts were made to relate swelling power to a variety of physico-chemical constants, such attempts were generally not fruitful. The reason for this situation lies in the fact that the nonaqueous systems were not chosen on the basis of their physico-chemical constants such as boiling point, dipole moment, molar volume, etc. It became evident early in the experimental work that it is necessary that a nonaqueous system be capable of disrupting the native cotton cellulose hydrogen bonding network. In line with this observation, attention was given to nonaqueous systems containing components capable of such disruption. Physico-Chemical constants for the binary systems which were studied during the course of this work are not available in the literature, and their evaluation would represent a research program of its own. Therefore relationships between swelling power and physico-chemical constants other than those referred to in the previous chapters could not be established.

Several important observations were made and these are discussed in summary form below, with recommendations for further research.

1. The introduction of solutes, whose structure would suggest hydrogen bonding capacity, into organic solvents, greatly increases the extent of interaction between the binary system and the cotton cellulose, relative to the pure solvent. Such solutes are exemplified by citric acid, tartaric acid, urea, and polyhydric alcohols. It is recommended that other solutes be investigated and that attention be given to studying the absorption of various solutes from solution.

2. The results which were obtained with cyclohexanone, cyclohexanol, and glucosepentaacetate solutions in various solvents, suggest the importance of molecular shape and configuration. It may be speculated that certain organic molecules are able to penetrate and be retained by cotton cellulose on the basis of their favorable molecular configuration and conformation rather than upon the basis of their functionality. It is strongly recommended that this approach be fully explored.

3. The concept of forming a cellulose derivative and subsequently removing the added group in order to form a more open or reactive cellulosic structure seems to hold some promise. The data which were obtained using a formylation followed by a saponification technique suggest some desirable effects. It is suggested that this approach be explored and that more complete substitution be achieved during the derivative formation.

4. It was observed that mercerized cotton which was dried by an organic solvent replacement technique gave evidence of greater reactivity than a mercerized sample dried by normal heating method. It is recommended that solvent replacement drying be thoroughly investigated as a pretreatment for a more highly reactive cotton cellulose.

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